

Diastereo- and Enantioselective Iridium-catalyzed Allylation of Cyclic Ketone Enolates: Synergetic Effect of Ligands and Barium Enolates

Wenyong Chen, Ming Chen, and John F. Hartwig*

Department of Chemistry, University of California, Berkeley, California, 94720, United States

Supporting Information

Table of Contents

General Experimental Details	S-1
General Procedure for Evaluating the Conditions for Allylation of 2-Methyl-1-tetralone	S-2
General Procedure for Ir-Catalyzed Allylation of Ketones	S-3
Procedures for the Transformations of Allylated Ketones	S-15
References	S-18
X-ray diffraction study of S1	S-19
X-ray diffraction study of S2	S-32
¹ H and ¹³ C NMR Spectra for All New Compounds	S-39

General Experimental Details

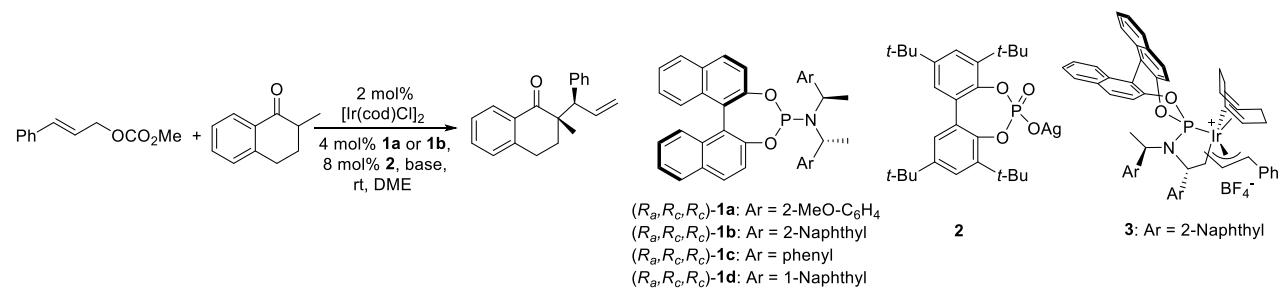
All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by standard Schlenk techniques. DCM, toluene, THF were degassed by purging with argon for 15 minutes and dried with a solvent purification system containing a one-meter column of activated alumina. Cinnamyl alcohol, 4-nitrocinnamyl alcohol, 4-methoxybenzaldehyde, 4-fluorobenzaldehyde, 3-fluorobenzaldehyde and 4-chlorobenzaldehyde were purchased from Sigma-Aldrich and used without further purification. Vinylmagnesium chloride was purchased as a 1.6 M solution in THF from Sigma-Aldrich. Substituted ketones were prepared according to literature procedures.¹ All the allylic carbonates and acetates were prepared according to literature procedures.² The racemic samples were prepared by running reactions with a racemic catalyst.

[Ir(cod)Cl]₂ was obtained from Johnson-Matthey and used without further purification. GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 m film) and an FID detector. HPLC analyses were conducted on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector) with chiral stationary columns (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High-resolution mass spectra were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. NMR spectra were acquired on Bruker AV-500, DRX-500, and AV-600 spectrometers. Chemical shifts were reported in ppm relative to a residual solvent peak (CDCl₃ = 7.26 ppm for ¹H and 77.00 ppm for ¹³C). Coupling constants were reported in hertz. Flash column chromatography was performed on Silicyle Silica-P silica gel. Products were visualized on TLC plates by UV or by staining with KMnO₄.

General Procedure for Evaluating the Conditions of Allylation of 2-Methyl-1-tetralone

In a nitrogen-filled dry-box, the cinnamyl carbonate (0.125 mmol, 1.00 equiv), $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.00250 mmol, 0.0200 equiv), ligand (0.00500 mmol, 0.0400 equiv), **2** (0.0200 mmol, 0.0800 equiv) and solvent (0.300 mL) were added to a 1-dram vial. The mixture was stirred for 20 min before 2-methyl-1-tetralone (0.1500 mmol, 1.20 equiv) and base (0.1500 mmol, 1.20 equiv) were added. The vial was sealed with a cap containing a PTFE-lined silicone-septum, removed from the dry-box, and stirred at room temperature for 10 h. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was concentrated under reduced pressure. CDCl_3 (0.7-0.8 mL) was added to dissolve the crude reaction mixture, and mesitylene (23 μL) was added as an internal standard. The diastereoselectivity was then determined by ^1H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 6:1) to yield the product.

Table 1. Evaluation of the Effect of Ligand and Metal Enolates on the Ir-Catalyzed Allylation of 2-methyl-1-tetralone^a



Entry	ligand	Solvent	Base	Yield(%) ^b	dr ^c	ee(%) ^d
1	1a	DME	None	0	-	-
2	1a	DME	LHMDS	74	2.0:1	-
3	1b	DME	LHMDS	70	2.3:1	-
4	1a	DME	Mg(Ot-Bu)_2	10	1.1:1	-
5	1a	DME	Ca(Oi-Pr)_2	17	1.3:1	-
6	1a	DME	Sr(Oi-Pr)_2	64	1.7:1	-
7	1a	DME	Ba(Ot-Bu)_2	75	2.0:1	-
8	1b	DME	Mg(Ot-Bu)_2	15	1.6:1	-
9	1b	DME	Ca(Oi-Pr)_2	20	3.3:1	-
10	1b	DME	Sr(Oi-Pr)_2	61	4.5:1	-
11	1b	DME	Ba(Ot-Bu)_2	72	5.0:1	98%
12 ^e	1b	THF	Ba(Ot-Bu)_2	83	9.0:1	98%
13 ^{e,f}	1b	THF	Ba(Ot-Bu)_2	82(81)	11:1	98%
14 ^{e,f,g}	1b	THF	Ba(Ot-Bu)_2	83(81)	11:1	98%

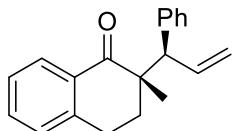
15	1b	DCM	Ba(O <i>t</i> -Bu) ₂	73	5:1	-
16	1b	Toluene	Ba(O <i>t</i> -Bu) ₂	49	3.8:1	-
17	1b	Dioxane	Ba(O <i>t</i> -Bu) ₂	74	4.4:1	-
18	1b	CPME	Ba(O <i>t</i> -Bu) ₂	64	4.1:1	-
19	1b	DME	NaHMDS	70	2.2:1	-
20	1b	DME	KHMDS	64	2:1	-
21	1c	DME	Ba(O <i>t</i> -Bu) ₂	80	4.2:1	-
22	1d	DME	Ba(O <i>t</i> -Bu) ₂	70	4.6:1	-

^a1.00 equiv of cinnamyl carbonate, 1.20 equiv of 2-methyl-1-tetralone. Absolute configuration of the allylation product was determined by analogy. ^bDetermined by ¹H NMR analysis with mesitylene as the internal standard. Numbers in parentheses correspond to isolated yield. ^cDetermined by ¹H NMR analysis of crude reaction mixtures. ^dDetermined by chiral HPLC analysis of the major diastereomer. ^eTHF instead of DME. ^fThe reaction was conducted at 5 °C. ^gPreformed catalyst **3** was used instead of the in situ generated catalyst.

General Procedure for Ir-catalyzed Allylation of Ketones

In a nitrogen-filled dry-box, the ketone (0.1500 mmol, 1.20 equiv) and Ba(*t*-OBu)₂ (0.1500 mmol, 1.20 equiv) were added to a 1-dram vial containing THF (0.2 mL). While the mixture was stirred for 20-30 minutes at RT, the allyl carbonate (0.125 mmol, 1.00 equiv) and complex **3** (0.00250 mmol, 0.0200 equiv) were added to another 1-dram vial containing THF (0.2 mL). Both vials were sealed with a cap containing a septum and removed from the dry-box. After cooling both solutions to 5 °C, the barium ketone enolate was transferred into the vial containing the allyl carbonate via syringe. The reaction mixture was maintained at 5 °C and stirred for 10 h. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the reaction was quenched by 1 mL saturated solution of potassium sodium tartrate. After stirring for 20 minutes, the mixture was poured into a separatory funnel containing EtOAc (3 mL), and the layers were separated. The aqueous layer was extracted by EtOAc (2 x 2 mL), and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. CDCl₃ (0.7-0.8 mL) was added to dissolve the crude reaction mixture. The diastereoselectivity was then determined by ¹H NMR spectroscopy. After this analysis, the crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 6:1) to yield the product.

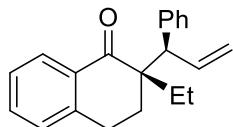
(S)-2-methyl-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-methyl-1-tetralone (24.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 81% yield (27.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 19.5 min (major); t_R 38.9 min (minor) [(Chiralcel OJ-H) hexane/*i*-PrOH, 99.7:0.3, 1.0 mL/min] to be >99%. [α]_D²⁵ = -43.3 (c 0.60, CH₂Cl₂). ¹H NMR (500 MHz, CDCl₃) δ 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 (td,

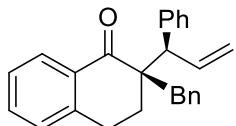
$J = 7.4, 1.5$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.32 – 7.20 (m, 4H), 7.20 – 7.12 (m, 2H), 6.27 (dt, $J = 17.8, 9.0$ Hz, 1H), 5.15 (d, $J = 12.0$ Hz, 1H), 5.14 (d, $J = 15.5$ Hz, 1H), 4.03 (d, $J = 8.5$ Hz, 1H), 3.20 – 2.82 (m, 2H), 2.35 (ddd, $J = 13.9, 9.0, 5.2$ Hz, 1H), 1.95 (dt, $J = 13.5, 5.6$ Hz, 1H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 201.5, 143.0, 140.2, 137.4, 133.1, 132.5, 129.7, 128.5, 128.1, 127.9, 126.8, 126.6, 117.8, 54.5, 48.9, 30.8, 25.0, 20.8. HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{21}\text{O} ([\text{M}+\text{H}]^+)$: 277.1587. Found: 277.1589.

(S)-2-ethyl-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-ethyl-1-tetralone (26.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and $\text{Ba}(t\text{-OBu})_2$ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 92% yield (33.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 12.3 min (major); t_R 17.9 min (minor) [(Chiralcel OD-H) hexane/i-PrOH, 99.8:0.2, 1.0 mL/min] to be 95%. $[\alpha]_D^{25} = -34.0$ (c 0.30, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 8.06 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.45 (dd, $J = 8.0, 6.5$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.28 – 7.22 (m, 2H), 7.20 (d, $J = 7.5$ Hz, 2H), 7.18 – 7.11 (m, 2H), 6.41 (ddd, $J = 16.6, 10.3, 8.6$ Hz, 1H), 5.12 (d, $J = 10.2$ Hz, 1H), 5.09 (d, $J = 18.6$ Hz, 1H), 3.93 (d, $J = 8.6$ Hz, 1H), 2.96 (t, $J = 6.4$ Hz, 2H), 2.20 (dt, $J = 13.9, 7.4$ Hz, 1H), 2.15 (dt, $J = 13.9, 6.0$ Hz, 1H), 1.69 (dq, $J = 14.3, 7.1$ Hz, 1H), 1.61 (dq, $J = 14.3, 7.1$ Hz, 1H), 0.84 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.4, 142.8, 140.6, 138.4, 132.9, 129.75, 129.74, 128.5, 127.97, 127.95, 126.6, 126.5, 117.0, 53.7, 51.9, 28.3, 25.3, 25.1, 8.3. HRMS (ESI) Calcd. for $\text{C}_{21}\text{H}_{23}\text{O} ([\text{M}+\text{H}]^+)$: 291.1743. Found: 291.1745.

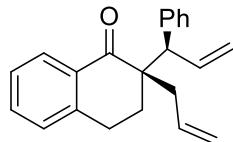
(R)-2-benzyl-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and $\text{Ba}(t\text{-OBu})_2$ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 87% yield (45.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 14.5 min (major); t_R 13.8 min (minor) [(Chiralcel OD-H) hexane/i-PrOH, 99.6:0.4, 1.0 mL/min] to be >99%. $[\alpha]_D^{25} = +27.6$ (c 3.0, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3) δ 8.06 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.44 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.38 – 7.22 (m, 4H), 7.12–7.18 (m, 6H), 7.09 (dd, $J = 8.0, 1.6$ Hz, 2H), 6.50 (dt, $J = 16.8, 9.7$ Hz, 1H), 5.26 (d, $J = 12.0$ Hz, 1H), 5.32 (d, $J = 19.2$ Hz, 1H), 3.86 (d, $J = 9.2$ Hz, 1H), 3.58 (d, $J = 13.2$ Hz, 1H), 3.02 (ddd, $J = 17.2, 10.4, 5.0$ Hz, 1H), 2.72 – 2.50 (m, 2H), 2.20 (dt, $J = 14.1, 5.0$ Hz, 1H), 1.98 (ddd, $J = 14.1, 10.5, 5.3$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.9, 143.0, 140.0, 138.2, 137.0, 133.2, 133.0, 130.9, 129.5, 128.5, 128.0, 127.9,

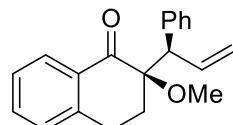
126.9, 126.6, 126.2, 118.2, 54.8, 53.2, 39.4, 28.9, 25.1. HRMS (ESI) Calcd. for $C_{26}H_{25}O$ ($[M+H]^+$): 353.1900. Found: 353.1902.

(R)-2-allyl-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



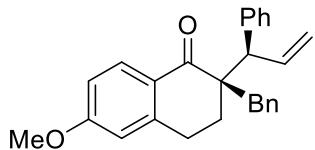
Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-allyl-1-tetralone (28.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and $Ba(t\text{-OBu})_2$ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 92% yield (34.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 12.8 min (major); t_R 19.6 min (minor) [(Chiralcel OD-H) hexane/i-PrOH, 99.8:0.2, 1.0 mL/min] to be 95%. $[\alpha]_D^{25} = -51.5$ (c 0.33, CH_2Cl_2). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, $J = 7.8$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.29 – 7.21 (m, 4H), 7.16 – 7.11 (m, 2H), 6.45 (dt, $J = 16.8, 9.7$ Hz, 1H), 5.71 (dtd, $J = 17.4, 8.5, 6.3$ Hz, 1H), 5.17 (d, $J = 10.5$ Hz, 1H), 5.14 (d, $J = 17.0$ Hz, 1H), 5.05 (d, $J = 15.0$ Hz, 1H), 5.04 (d, $J = 11.5$ Hz, 1H), 3.87 (d, $J = 9.0$ Hz, 1H), 2.98 (t, $J = 6.4$ Hz, 2H), 2.58 (dd, $J = 14.1, 6.3$ Hz, 1H), 2.27 (dd, $J = 14.1, 8.2$ Hz, 1H), 2.14–2.22 (q, $J = 6.3$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 200.1, 142.9, 140.3, 137.8, 134.1, 133.0, 132.8, 129.6, 128.6, 127.9, 126.7, 126.5, 118.2, 117.5, 54.5, 51.7, 37.9, 28.9, 25.0. HRMS (ESI) Calcd. for $C_{22}H_{23}O$ ($[M+H]^+$): 303.1743. Found: 303.1745.

(R)-2-methoxy-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



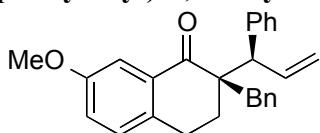
Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-methoxy-1-tetralone (26.4 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and $Ba(t\text{-OBu})_2$ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 82% yield (29.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 17.3 min (major); t_R 21.5 min (minor) [(Chiralcel OD-H) hexane/i-PrOH, 99.6:0.4, 1.0 mL/min] to be 99%. $[\alpha]_D^{25} = +2.1$ (c 3.3, CH_2Cl_2). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.96 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.50 (td, $J = 7.5, 1.5$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.29 – 7.20 (m, 4H), 7.20 – 7.12 (m, 2H), 6.27 (dt, $J = 17.4, 9.3$ Hz, 1H), 5.21 (d, $J = 15.6$ Hz, 1H), 5.19 (d, $J = 11.5$ Hz, 1H), 4.08 (d, $J = 8.9$ Hz, 1H), 3.30 (s, 3H), 3.16 (dt, $J = 17.4, 5.7$ Hz, 1H), 3.08 (ddd, $J = 17.6, 8.6, 5.3$ Hz, 1H), 2.55 (ddd, $J = 13.7, 8.4, 5.5$ Hz, 1H), 2.29 (dt, $J = 13.5, 5.6$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 195.4, 142.8, 139.3, 136.8, 133.3, 132.6, 129.5, 128.5, 128.0, 127.9, 126.75, 126.73, 117.7, 82.0, 51.6, 51.3, 28.8, 25.5. HRMS (EI) Calcd. for $C_{19}H_{16}O$ ($[M-\text{CH}_3\text{OH}]^+$): 260.1201. Found: 260.1206.

(R)-2-benzyl-6-methoxy-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



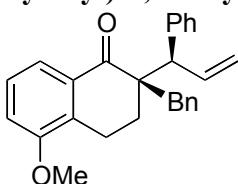
Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-7-methoxy-1-tetralone (39.9 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 95% yield (45.4 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R 28.2 min (major); *t*_R 24.1 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.5:0.5, 1.0 mL/min] to be >99%. [α]_D²⁵ = +62.7 (c 1.1, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.8 Hz, 1H), 7.38 – 7.21 (m, 3H), 7.09–7.18 (m, 7H), 6.84 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.48 (ddd, *J* = 16.9, 10.3, 9.1 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.19 (d, *J* = 17.3 Hz, 1H), 3.84 (s, 3H), 3.56 (d, *J* = 13.2 Hz, 1H), 2.94 (ddd, *J* = 17.1, 10.1, 4.9 Hz, 1H), 2.56 (d, *J* = 13.1 Hz, 1H), 2.51 (dt, *J* = 14.1, 5.9 Hz, 1H), 2.17 (dt, *J* = 14.1, 5.2 Hz, 1H), 1.96 (ddd, *J* = 14.0, 10.1, 5.2 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 198.7, 163.3, 145.5, 140.2, 138.3, 137.3, 130.8, 130.4, 129.6, 127.99, 127.92, 127.0, 126.8, 126.10, 117.9, 113.3, 112.0, 55.4, 55.3, 52.9, 39.9, 29.0, 25.6. HRMS (ESI) Calcd. for C₂₇H₂₇O₂ ([M+H]⁺): 383.2006. Found: 383.2010.

(R)-2-benzyl-7-methoxy-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



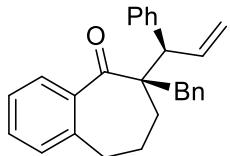
Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-7-methoxy-1-tetralone (40.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 50:1 to 15:1) to give the title compound as a colorless oil in 82% yield. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R = 31.7 min (major); *t*_R = 34.9 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.8:0.2, 1.0 mL/min] to be >99%; [α]_D²⁵ = +39.7 (c 1.5, CH₂Cl₂); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 2.5 Hz, 1H), 7.29–7.22 (m, 4H), 7.15–7.08 (m, 4H), 7.06–6.99 (m, 4H), 6.46 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 5.23 (dd, *J* = 10.0, 1.0 Hz, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 3.85 (s, 3H), 3.86–3.83 (m, 1H), 3.55 (d, *J* = 13.0 Hz, 1H), 2.94 (ddd, *J* = 16.5, 10.5, 5.0 Hz, 1H), 2.57 (d, *J* = 13.5 Hz, 1H), 2.52 (dt, *J* = 17.0, 5.0 Hz, 1H), 2.14 (dt, *J* = 14.5, 5.0 Hz, 1H), 1.93 (ddd, *J* = 15.0, 10.5, 5.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 200.0, 158.7, 140.4, 138.5, 137.4, 135.9, 134.2, 131.2, 130.0, 129.9, 128.3, 128.2, 127.2, 126.4, 121.7, 118.4, 110.2, 55.8, 55.1, 53.4, 39.7, 29.5, 24.6; HRMS (ESI) Calcd. for C₂₇H₂₇O₂ ([M+H]⁺): 383.2006. Found: 383.2004.

(R)-2-benzyl-5-methoxy-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one



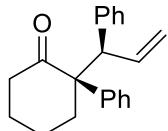
Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-5-methoxy-1-tetralone (40.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 50:1 to 15:1) to give the title compound as a colorless oil in 88% yield. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R = 11.3 min (minor); *t*_R = 12.7 min (major) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.0:1.0, 1.0 mL/min] to be 98%; [α]_D²⁵ = +25.9 (c 1.0, CH₂Cl₂); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.32-7.25 (m, 4H), 7.18-7.12 (m, 5H), 7.04-7.00 (m, 3H), 6.53 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 5.26 (d, *J* = 17.0 Hz, 1H), 3.86 (s, 3H), 3.87-3.83 (m, 1H), 3.57 (d, *J* = 13.5 Hz, 1H), 2.88 (ddd, *J* = 16.0, 11.0, 5.5 Hz, 1H), 2.76 (dt, *J* = 16.5, 5.0 Hz, 1H), 2.62 (d, *J* = 13.0 Hz, 1H), 2.17 (dt, *J* = 14.0, 4.5 Hz, 1H), 1.89 (ddd, *J* = 14.5, 11.0, 6.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 199.8, 156.9, 140.4, 138.6, 137.2, 134.2, 132.3, 131.4, 129.8, 128.2, 128.1, 127.3, 127.1, 126.4, 120.0, 118.6, 114.0, 55.9, 54.2, 53.1, 38.4, 28.7, 19.1; HRMS (ESI) Calcd. for C₂₇H₂₇O₂ ([M+H]⁺): 383.2006. Found: 383.2004.

(R)-6-benzyl-6-((R)-1-phenylallyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-1-benzosuberone (37.2 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 95% yield (43.4 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R 11.5 min (major); *t*_R 10.5 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.4:0.6, 1.0 mL/min] to be >99%. [α]_D²⁵ = +8.3 (c 2.2, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.09 (m, 13H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.47 (dt, *J* = 16.9, 9.8 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 5.15 (d, *J* = 16.9 Hz, 1H), 3.89 (d, *J* = 9.3 Hz, 1H), 3.45 (d, *J* = 13.2 Hz, 1H), 2.81 (dt, *J* = 14.6, 7.2 Hz, 1H), 2.72 (d, *J* = 13.2 Hz, 1H), 2.52 (dt, *J* = 14.2, 6.6 Hz, 1H), 2.01 (dt, *J* = 13.3, 6.6 Hz, 1H), 1.92 (t, *J* = 6.2 Hz, 2H), 1.81 (dt, *J* = 13.7, 6.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 212.1, 141.6, 140.4, 137.8, 137.8, 137.7, 131.3, 130.9, 130.0, 129.3, 128.2, 128.1, 127.8, 126.8, 126.3, 126.1, 118.3, 58.3, 58.0, 43.3, 32.3, 29.8, 23.6. HRMS (ESI) Calcd. for C₂₇H₂₇O ([M+H]⁺): 367.2056. Found: 367.2065.

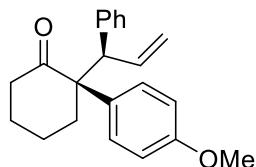
(S)-2-phenyl-2-((R)-1-phenylallyl)cyclohexan-1-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-phenylcyclohexanone (26.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 81% yield (29.4 mg).

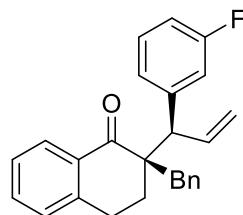
The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.3 min (major); t_R 7.4 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.6:0.4, 1.0 mL/min] to be >99%. $[\alpha]_D^{25} = -151.0$ (c 2.0, CH₂Cl₂). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.13–7.18 (m, 3H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.98 – 6.91 (m, 2H), 5.96 (dt, *J* = 18.0, 9.6 Hz, 1H), 4.95 (d, *J* = 18.0 Hz, 1H), 4.93 (d, *J* = 9.6 Hz, 1H), 4.00 (d, *J* = 8.8 Hz, 1H), 2.41 (td, *J* = 13.0, 6.0 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.29 – 2.21 (m, 1H), 1.89 – 1.77 (m, 2H), 1.71 – 1.57 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 212.6, 140.9, 138.3, 138.0, 130.4, 128.9, 128.1, 127.5, 126.9, 126.2, 116.6, 61.3, 56.6, 40.6, 35.4, 28.6, 21.4. HRMS (ESI) Calcd. for C₂₁H₂₃O ([M+H]⁺): 291.1743. Found: 291.1749.

(S)-2-(4-methoxyphenyl)-2-((R)-1-phenylallyl)cyclohexan-1-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-anisylcyclohexanone (30.6 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 85% yield (34.0 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.8 min (major); t_R 14.0 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.5:0.5, 1.0 mL/min] to be >99%. $[\alpha]_D^{25} = -149.3$ (c 0.9, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.15–7.21 (m, 3H), 7.02 – 6.83 (m, 6H), 5.96 (dt, *J* = 16.3, 9.5 Hz, 1H), 4.97 (d, *J* = 17.0 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.01 (d, *J* = 8.8 Hz, 1H), 3.85 (s, 3H), 2.48–2.40 (m, 1H), 2.28–2.21 (m, 2H), 1.85–1.92 (m, 1H), 1.84 – 1.73 (m, 1H), 1.73 – 1.51 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 212.9, 158.4, 140.9, 138.5, 130.3, 130.0, 127.5, 126.2, 116.5, 113.4, 60.6, 56.4, 55.2, 40.4, 35.7, 28.6, 21.3. HRMS (ESI) Calcd. for C₂₂H₂₅O₂ ([M+H]⁺): 321.1849. Found: 321.1852.

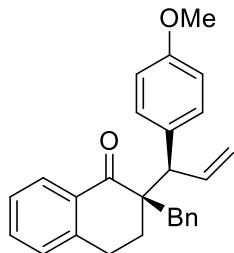
(R)-2-benzyl-2-((R)-1-(3-fluorophenylallyl)-3,4-dihydroronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl 3-fluorocinnamyl carbonate (26.3 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 87% yield (40.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 23.7 min (major); t_R 27.5 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.8:0.2, 1.0 mL/min] to be >99%. $[\alpha]_D^{25} = +47.3$ (c 1.1, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.15 (t, *J* = 6.0 Hz, 6H), 6.95 (td, *J* = 8.4, 2.5 Hz, 1H), 6.87 – 6.75 (m, 2H), 6.45 (dt, *J* = 16.8, 9.7 Hz, 1H), 5.28 (d, *J*

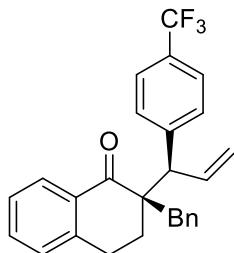
= 10.0 Hz, 1H), 5.23 (d, J = 16.8 Hz, 1H), 3.85 (d, J = 9.1 Hz, 1H), 3.56 (d, J = 13.2 Hz, 1H), 3.00 (ddd, J = 17.5, 10.2, 4.9 Hz, 1H), 2.60 (dt, J = 17.5, 5.5 Hz, 1H), 2.58 (d, J = 13.0 Hz, 1H), 2.18 (dt, J = 14.1, 5.1 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 199.7, 162.4 (d, J = 245.4 Hz), 142.9, 142.7 (d, J = 6.8 Hz), 137.9, 136.4, 133.2, 133.0, 130.8, 129.4 (d, J = 8.3 Hz), 128.6, 128.1, 128.0, 126.8, 126.3, 125.3 (d, J = 2.6 Hz), 118.7, 116.4 (d, J = 21.5 Hz), 113.8 (d, J = 20.9 Hz), 54.3, 53.1, 39.2, 28.9, 24.9. HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{24}\text{OF}$ ($[\text{M}+\text{H}]^+$): 371.1806. Found: 371.1810.

(R)-2-benzyl-2-((R)-1-(4-methoxyphenyl)allyl)-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl 4-methoxycinnamyl carbonate (27.8 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and $\text{Ba}(t\text{-OBu})_2$ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 85% yield (45.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 48.3 min (major); t_R 58.3 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.8:0.2, 1.0 mL/min] to be >99%. $[\alpha]_D^{25} = +100.7$ (c 1.5, CH_2Cl_2). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.06 (dd, J = 7.9, 1.5 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.37 – 7.25 (m, 2H), 7.21 – 7.04 (m, 5H), 7.06 – 6.97 (m, 2H), 6.92 – 6.80 (m, 2H), 6.46 (ddd, J = 16.8, 10.2, 8.9 Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 5.20 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H), 3.58 (d, J = 13.2 Hz, 1H), 3.03 (ddd, J = 17.5, 10.3, 4.9 Hz, 1H), 2.60 (dt, J = 12.8, 5.3 Hz, 1H), 2.58 (d, J = 13.0 Hz, 1H), 2.18 (dt, J = 14.1, 5.0 Hz, 1H), 1.97 (ddd, J = 14.1, 10.4, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 200.1, 158.3, 143.0, 138.3, 137.2, 133.2, 133.0, 132.0, 130.9, 130.4, 128.6, 128.0, 127.9, 126.7, 126.1, 117.9, 113.4, 55.2, 53.9, 53.3, 39.3, 28.9, 25.1. HRMS (ESI) Calcd. for $\text{C}_{27}\text{H}_{27}\text{O}_2$ ($[\text{M}+\text{H}]^+$): 383.2006. Found: 383.2013.

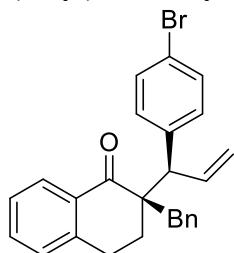
(R)-2-benzyl-2-((R)-1-(4-(trifluoromethyl)phenyl)allyl)-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl 4-trifluoromethylcinnamyl carbonate (32.5 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and $\text{Ba}(t\text{-OBu})_2$ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 92%

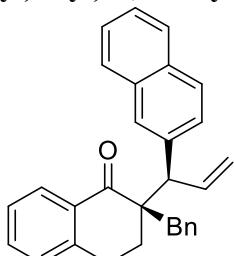
yield (48.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 13.2 min (major); t_R 14.9 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.8:0.2, 1.0 mL/min] to be >99%. $[\alpha]_D^{25} = +39.5$ (c 1.1, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.20-7.10 (m, 8H), 6.51 (dt, *J* = 16.9, 9.7 Hz, 1H), 5.31 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.24 (d, *J* = 16.9 Hz, 1H), 3.90 (d, *J* = 9.1 Hz, 1H), 3.52 (d, *J* = 13.1 Hz, 1H), 3.04 (ddd, *J* = 17.6, 10.4, 5.0 Hz, 1H), 2.65 (dt, *J* = 17.5, 5.5 Hz, 1H), 2.61 (d, *J* = 13.2 Hz, 1H), 2.18 (dt, *J* = 14.2, 5.0 Hz, 1H), 1.99 (ddd, *J* = 14.1, 10.4, 5.2 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 199.4, 144.3, 142.9, 137.7, 136.2, 133.3, 130.9, 129.8, 128.9 (q, *J* = 32.6 Hz), 128.6, 128.0, 128.0, 126.8, 126.32, 124.9 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.4 Hz), 119.0, 54.1, 53.0, 38.8, 29.0, 24.9. HRMS (ESI) Calcd. for C₂₁H₂₄OF₃ ([M+H]⁺): 421.1774. Found: 421.1783.

(R)-2-benzyl-2-((R)-1-(4-bromophenyl)allyl)-3,4-dihydronaphthalen-1(2H)-one



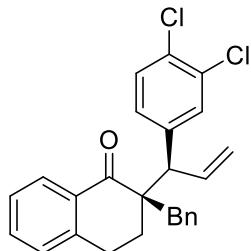
Prepared according to the general procedure using methyl 4-bromocinnamyl carbonate (34.0 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 95% yield (51.1 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 45.4 min (major); t_R 35.9 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.95:0.05, 1.0 mL/min] to be >99%. $[\alpha]_D^{25} = +106.2$ (c 1.3, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.30 (m, 1H), 7.18-7.11 (m, 6H), 6.99 – 6.88 (m, 2H), 6.46 (ddd, *J* = 16.8, 10.2, 9.1 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 3.81 (d, *J* = 9.1 Hz, 1H), 3.53 (d, *J* = 13.2 Hz, 1H), 3.02 (ddd, *J* = 16.5, 10.0, 5.0 Hz, 1H), 2.62 (dt, *J* = 17.0, 4.5 Hz, 1H), 2.58 (d, *J* = 13.2 Hz, 1H), 2.16 (dt, *J* = 14.1, 5.0 Hz, 1H), 1.97 (ddd, *J* = 14.0, 10.4, 5.2 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 199.6, 142.9, 139.2, 137.8, 136.5, 133.2, 132.9, 131.2, 131.1, 130.9, 128.6, 128.0, 128.0, 126.8, 126.3, 120.8, 118.6, 53.8, 53.0, 38.9, 28.9, 24.9. HRMS (ESI) Calcd. for C₂₆H₂₄OBr ([M+H]⁺): 431.1005. Found: 431.1014.

(R)-2-benzyl-2-((R)-1-(naphthalen-2-yl)allyl)-3,4-dihydronaphthalen-1(2H)-one



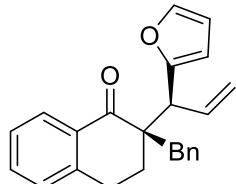
Prepared according to the general procedure using methyl 3-(2-naphthyl)allyl carbonate (30.3 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 82% yield (41.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R 18.3 min (major); *t*_R 15.9 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.6:0.4, 1.0 mL/min] to be 99%. [α]_D²⁵ = +112.7 (c 1.5, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.85–7.76 (m, 3H), 7.62 – 7.43 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.15 (br s, 6H), 6.62 (dt, *J* = 17.1, 9.5 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 4.06 (d, *J* = 8.9 Hz, 1H), 3.64 (d, *J* = 13.3 Hz, 1H), 3.04 (ddd, *J* = 15.9, 10.0, 5.1 Hz, 1H), 2.69 (d, *J* = 13.5 Hz, 1H), 2.63 (dt, *J* = 18.0, 5.0 Hz, 1H), 2.40 – 2.22 (m, 1H), 2.17 – 1.95 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 200.1, 143.0, 138.1, 137.7, 137.1, 133.3, 133.1, 133.0, 132.3, 130.8, 128.5, 128.4, 127.97, 127.92, 127.78, 127.75, 127.5, 127.4, 126.6, 126.1, 125.9, 125.6, 118.3, 55.1, 53.37, 39.8, 29.0, 25.1. HRMS (ESI) Calcd. for C₃₀H₂₇O ([M+H]⁺): 403.2056. Found: 403.2063.

(R)-2-benzyl-2-((R)-1-(3,4-dichlorophenyl)allyl)-3,4-dihydronaphthalen-1(2H)-one



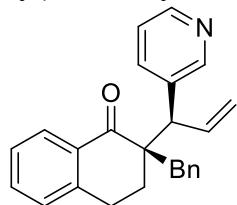
Prepared according to the general procedure using methyl 3,4-dichlorocinnamyl carbonate (32.8 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as white wax in 93% yield (48.8 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R 9.6 min (major); *t*_R 8.8 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99:1, 1.0 mL/min] to be 98%. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.44 (td, *J* = 7.4, 1.5 Hz, 1H), 7.30–7.34 (m, 2H), 7.21 – 7.04 (m, 7H), 6.85 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.41 (dt, *J* = 16.8, 9.7 Hz, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 3.77 (d, *J* = 9.0 Hz, 1H), 3.49 (d, *J* = 13.2 Hz, 1H), 2.99 (ddd, *J* = 17.5, 10.2, 5.0 Hz, 1H), 2.63 (dt, *J* = 17.4, 5.4 Hz, 1H), 2.56 (d, *J* = 13.2 Hz, 1H), 2.13 (dt, *J* = 14.2, 5.0 Hz, 1H), 1.96 (ddd, *J* = 14.8, 10.2, 5.3 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 199.4, 142.8, 140.5, 137.5, 135.9, 133.2, 132.7, 131.9, 131.3, 130.85, 130.81, 129.8, 128.9, 128.5, 128.0, 127.9, 126.8, 126.3, 119.06, 53.51, 52.9, 38.9, 28.9, 24.8. HRMS (ESI) Calcd. for C₂₆H₂₃OCl₂ ([M+H]⁺): 421.1120. Found: 421.1129.

(R)-2-benzyl-2-((S)-1-(furan-2-yl)allyl)-3,4-dihydronaphthalen-1(2H)-one



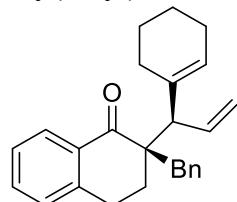
Prepared according to the general procedure using methyl 3-(2-furyl)allyl carbonate (22.8 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 79% yield (33.8 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R 11.0 min (major); *t*_R 10.3 min (minor) [(Chiralpak AD-H) heptane/*i*-PrOH, 99:1, 1.0 mL/min] to be 98%. [α]_D²⁵ = +2.6 (c 1.1, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.10 – 8.01 (m, 1H), 7.49 – 7.38 (m, 2H), 7.35 – 7.28 (m, 1H), 7.20 – 7.05 (m, 6H), 6.36 (s, 1H), 6.17 (dt, *J* = 18.5, 9.7 Hz, 1H), 6.09 (d, *J* = 3.5 Hz, 1H), 5.18 (d, *J* = 9.5 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 4.07 (d, *J* = 8.1 Hz, 1H), 3.45 (d, *J* = 13.6 Hz, 1H), 3.01 – 2.91 (m, 1H), 2.74–2.63 (m, 2H), 2.30–2.21 (m, 1H), 2.14–2.06 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 199.8, 153.7, 142.9, 141.5, 137.8, 135.0, 133.0, 130.6, 128.5, 127.99, 127.89, 126.6, 126.2, 118.4, 110.2, 108.2, 53.2, 48.4, 40.0, 28.7, 25.2. HRMS (ESI) Calcd. for C₂₄H₂₂O₂K ([M+K]⁺): 381.1257. Found: 381.1256.

(R)-2-benzyl-2-((R)-1-(pyridin-3-yl)allyl)-3,4-dihydronaphthalen-1(2H)-one



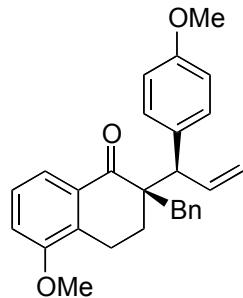
Prepared according to the general procedure using methyl 3-(3-pyridyl)allyl carbonate (24.2 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 3:1) to give the title compound as a colorless oil in 90% yield (39.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R 24.7 min (major); *t*_R 27.3 min (minor) [(Chiralcel OD-H) hexane/EtOH, 95:5, 0.6 mL/min] to be >99%. [α]_D²⁵ = +23.6 (c 2.0, CH₂Cl₂). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.48 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.27 (d, *J* = 2.2 Hz, 1H), 8.02 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.03 (m, 7H), 6.46 (ddd, *J* = 16.8, 10.2, 8.9 Hz, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 3.83 (d, *J* = 9.0 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H), 3.00 (ddd, *J* = 17.7, 10.3, 5.0 Hz, 1H), 2.63 (dt, *J* = 17.4, 5.2 Hz, 1H), 2.57 (d, *J* = 13.2 Hz, 1H), 2.16 (dt, *J* = 14.1, 5.0 Hz, 1H), 1.97 (ddd, *J* = 14.2, 10.3, 5.3 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 199.3, 150.6, 148.1, 142.8, 137.5, 136.7, 135.9, 135.7, 133.2, 130.8, 130.7, 128.5, 128.08, 127.98, 126.8, 126.2, 122.8, 119.0, 52.9, 51.9, 38.9, 28.8, 24.8. HRMS (ESI) Calcd. for C₂₅H₂₄NO ([M+H]⁺): 354.1852. Found: 354.1852. HRMS (ESI) Calcd. for C₂₆H₂₉O ([M+H]⁺): 357.2213. Found: 357.2222.

(R)-2-benzyl-2-((R)-1-(cyclohex-1-en-1-yl)allyl)-3,4-dihydronaphthalen-1(2H)-one



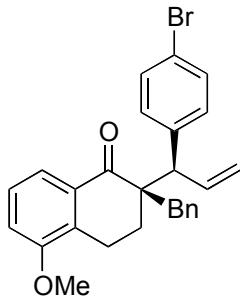
Prepared according to the general procedure using methyl 3-(1-cyclohexenyl)allyl carbonate (24.3 mg, 0.125 mmol), 2-benzyl-1-tetralone (35.1 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 10:1 to 6:1) to give the title compound as a colorless oil in 80% yield (35.6 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R 6.5 min (major); *t*_R 6.1 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.5:0.5, 1.0 mL/min] to be 99%. [α]_D²⁵ = +30.8 (c 0.4, CH₂Cl₂). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.35 – 7.26 (m, 1H), 7.26 – 7.08 (m, 6H), 6.28 (dt, *J* = 16.8, 9.7 Hz, 1H), 5.34 (br s, 1H), 5.18 (d, *J* = 9.7 Hz, 1H), 5.15 (d, *J* = 14.9 Hz, 1H), 3.72 (d, *J* = 13.3 Hz, 1H), 3.09 (d, *J* = 9.1 Hz, 1H), 3.02 (ddd, *J* = 17.5, 10.2, 5.0 Hz, 1H), 2.61 (dt, *J* = 17.5, 5.3 Hz, 1H), 2.59 (d, *J* = 13.4 Hz, 1H), 2.15 – 1.97 (m, 3H), 1.95 – 1.82 (m, 3H), 1.60 – 1.44 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 200.5, 142.9, 138.6, 137.3, 136.7, 133.2, 132.7, 130.9, 128.4, 127.9, 126.5, 126.1, 126.0, 116.5, 56.1, 52.6, 39.1, 29.3, 29.0, 25.4, 25.0, 23.0, 22.3. HRMS (EI) Calcd. for C₂₆H₂₈O ([M]⁺): 356.2140. Found: 356.2137.

(R)-2-benzyl-5-methoxy-2-((R)-1-(4-methoxyphenyl)allyl)-3,4-dihydronaphthalen-1(2H)-one



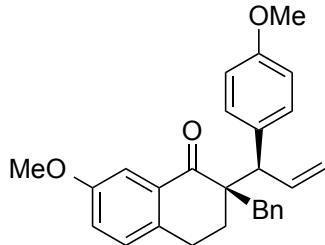
Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-5-methoxy-1-tetralone (40.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 30:1 to 10:1) to give the title compound as a colorless oil in 80% yield. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) *t*_R = 10.9 min (major); *t*_R = 12.1 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 98.0:2.0, 1.0 mL/min] to be 99%. [α]_D²⁵ = +48.0 (c 1.4, CH₂Cl₂); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.14 – 7.12 (m, 4H), 7.12 – 7.09 (m, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.46 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 5.20 (d, *J* = 17.0 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.79-3.77 (m, 1H), 3.52 (d, *J* = 13.0 Hz, 1H), 2.83 (ddd, *J* = 18.5, 11.0, 5.5 Hz, 1H), 2.72 (dt, *J* = 18.5, 5.5 Hz, 1H), 2.56 (d, *J* = 13.0 Hz, 1H), 2.11 (dt, *J* = 14.0, 4.5 Hz, 1H), 1.91 (ddd, *J* = 14.0, 10.5, 5.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 199.9, 158.6, 156.8, 138.6, 137.4, 134.2, 132.4, 132.3, 131.4, 130.6, 128.1, 127.2, 126.3, 120.0, 118.2, 114.0, 113.7, 55.9, 55.4, 53.2, 53.1, 38.3, 28.7, 19.1; HRMS (ESI) Calcd. for C₂₈H₂₉O₃ ([M+H]⁺): 413.2111. Found: 413.2110.

(R)-2-benzyl-2-((R)-1-(4-bromophenyl)allyl)-5-methoxy-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-5-methoxy-1-tetralone (40.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 50:1 to 15:1) to give the title compound as a colorless oil in 85% yield. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R = 5.25 min (major); t_R = 5.62 (minor) [(Chiralcel AS-H) hexane/*i*-PrOH, 95.0:5.0, 1.0 mL/min] to be 99%; [α]_D²⁵ = +61.9 (c 1.2, CH₂Cl₂); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.17 – 7.09 (m, 5H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.46 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 3.83 (s, 3H), 3.77 (d, *J* = 9.5 Hz, 1H), 3.48 (d, *J* = 13.0 Hz, 1H), 2.83 (ddd, *J* = 18.0, 10.5, 5.0 Hz, 1H), 2.74 (dt, *J* = 18.5, 5.0 Hz, 1H), 2.56 (d, *J* = 13.0 Hz, 1H), 2.10 (dt, *J* = 14.0, 4.5 Hz, 1H), 1.85 (ddd, *J* = 14.5, 11.0, 6.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 199.6, 156.9, 139.6, 138.2, 136.6, 133.9, 132.2, 131.4, 131.3, 128.2, 127.4, 126.5, 121.1, 120.0, 119.0, 114.2, 55.9, 53.3, 52.9, 38.0, 28.7, 19.0; HRMS (ESI) Calcd. for C₂₇H₂₅BrO₂ ([M+H]⁺): 461.1111. Found: 461.1112.

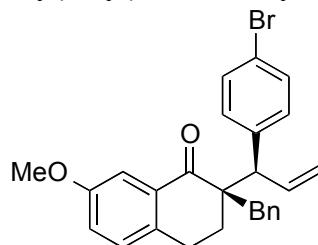
(R)-2-benzyl-7-methoxy-2-((R)-1-(4-methoxyphenyl)allyl)-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-7-methoxy-1-tetralone (40.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and Ba(*t*-OBu)₂ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 30:1 to 10:1) to give the title compound as a colorless oil in 76% yield. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R = 29.2 min (major); t_R = 35.0 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.0:1.0, 1.0 mL/min] to be 99%. [$\langle \rangle_D^{25}$] = +47.9 (c 1.0, CH₂Cl₂); ¹H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 2.5 Hz, 1H), 7.14 – 7.09 (m, 5H), 7.02 – 7.01 (m, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.42 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 5.16 (d, *J* = 17.0 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.81–3.76 (m, 1H), 3.52 (d, *J* = 13.5 Hz, 1H), 2.94 (ddd, *J* = 16.5, 10.5, 5.0

Hz, 1H), 2.55 (d, J = 13.5 Hz, 1H), 2.51 (dt, J = 17.0, 5.0 Hz, 1H), 2.12 (dt, J = 14.0, 5.0 Hz, 1H), 1.91 (ddd, J = 14.0, 10.0, 5.0 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 200.2, 158.7, 138.6, 137.6, 135.9, 134.2, 132.4, 131.5, 131.2, 130.8, 130.1, 128.2, 126.4, 121.7, 118.1, 113.7, 110.2, 55.9, 55.4, 54.2, 53.4, 39.6, 29.4, 23.6; HRMS (ESI) Calcd. for $\text{C}_{28}\text{H}_{29}\text{O}_3$ ($[\text{M}+\text{H}]^+$): 413.2111. Found: 413.2109.

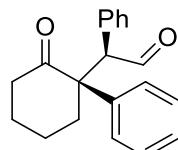
(R)-2-benzyl-2-((R)-1-(4-bromophenylallyl)-7-methoxy-3,4-dihydronaphthalen-1(2H)-one



Prepared according to the general procedure using methyl cinnamyl carbonate (24.0 mg, 0.125 mmol), 2-benzyl-7-methoxy-1-tetralone (40.0 mg, 0.150 mmol), **3** (2.9 mg, 0.0025 mmol) and $\text{Ba}(t\text{-OBu})_2$ (42.5 mg, 0.150 mmol). The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 50:1 to 15:1) to give the title compound as a colorless oil in 78% yield. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R = 14.3 min (major); t_R = 15.3 min (minor) [(Chiralcel OD-H) hexane/*i*-PrOH, 99.5:0.5, 1.0 mL/min] to be 99%; $[\alpha]_D^{25} = +53.3$ (c 1.5, CH_2Cl_2); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, J = 2.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.16-7.09 (m, 5H), 7.05-7.00 (m, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.42 (ddd, J = 17.0, 10.5, 10.0 Hz, 1H), 5.25 (d, J = 10.5 Hz, 1H), 5.18 (d, J = 17.0 Hz, 1H), 3.85 (s, 3H), 3.77 (d, J = 9.0 Hz, 1H), 3.49 (d, J = 13.0 Hz, 1H), 2.93 (ddd, J = 16.5, 10.0, 4.5 Hz, 1H), 2.55 (dt, J = 17.0, 5.0 Hz, 1H), 2.54 (d, J = 13.0 Hz, 1H), 2.10 (dt, J = 14.5, 5.0 Hz, 1H), 1.91 (ddd, J = 15.0, 10.5, 5.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 199.7, 158.7, 139.5, 138.1, 136.9, 135.8, 133.9, 131.5, 131.4, 131.2, 130.2, 128.3, 126.5, 121.9, 121.1, 118.9, 110.2, 55.8, 54.1, 53.2, 39.2, 29.5, 24.4; HRMS (ESI) Calcd. for $\text{C}_{27}\text{H}_{25}\text{BrO}_2$ ($[\text{M}+\text{H}]^+$): 461.1111. Found: 461.1109.

Procedures for the Transformations of Allylated Ketones

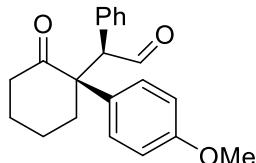
(R)-2-((S)-2-oxo-1-phenylcyclohexyl)-2-phenylacetaldehyde



NaIO_4 (158 mg, 0.74 mmol, 3.50 equiv) was dissolved in water (1.00 mL) in a 1-dram vial. A 2.5% solution of OsO_4 in *t*-BuOH (0.11 mL, 0.0105 mmol, 0.0500 equiv) and (S)-2-phenyl-2-((R)-1-phenylallyl)cyclohexan-1-one (60.0 mg, 0.211 mmol, 1.00 equiv) in ether (1.00 mL) were added to the vial sequentially. After sealing the vial with a cap containing a PTFE-lined silicone-septum, the reaction mixture was stirred at room temperature for 48 hours. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the reaction was

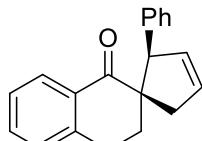
quenched by saturated Na_2SO_3 solution. The mixture was poured into a separatory funnel containing EtOAc (3 mL), and the layers were separated. The aqueous layer was extracted by EtOAc (2 x 2 mL), and the combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 3:1) to give the product as a colorless oil in 85% yield (51.0 mg). ^1H NMR (600 MHz, Chloroform- d) δ 10.02 (d, J = 2.6 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.19 (d, J = 7.3 Hz, 1H), 7.15 (t, J = 7.4 Hz, 2H), 6.92 (dd, J = 7.6, 2.1 Hz, 2H), 6.76 (dd, J = 7.3, 1.7 Hz, 2H), 3.94 (d, J = 2.6 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.45 – 2.34 (m, 1H), 2.00 – 1.86 (m, 2H), 1.79 – 1.54 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 212.8, 200.3, 136.3, 134.0, 131.3, 128.9, 128.3, 127.7, 127.6, 127.2, 63.9, 62.5, 40.0, 36.8, 28.4, 21.0. HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_2$ ($[\text{M}]^+$): 292.1463. Found: 292.1460.

(R)-2-((S)-1-(4-methoxyphenyl)-2-oxocyclohexyl)-2-phenylacetaldehyde



NaIO_4 (47.9 mg, 0.220 mmol, 3.50 equiv) was dissolved in water (0.50 mL) in a 1-dram vial. A 2.5% solution of OsO_4 in *t*-BuOH (0.032 mL, 0.00318 mmol, 0.0500 equiv) and (S)-2-(4-methoxyphenyl)-2-((R)-1-phenylallyl)cyclohexan-1-one (20.0 mg, 0.0640 mmol) in ether (0.50 mL) were added to the vial sequentially. After sealing the vial with a cap containing a PTFE-lined silicone-septum, the reaction mixture was stirred at room temperature for 48 hours. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the reaction was quenched by saturated Na_2SO_3 solution. The mixture was poured into a separatory funnel containing EtOAc (3 mL), and the layers were separated. The aqueous layer was extracted by EtOAc (2 x 2 mL), and the combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 3:1) to give the product as a colorless oil in 80% yield (16.0 mg). ^1H NMR (500 MHz, Chloroform- d) δ 10.02 (d, J = 2.6 Hz, 1H), 7.24 – 7.11 (m, 3H), 6.85 (br s, 4H), 6.82 – 6.69 (m, 2H), 3.96 (d, J = 2.7 Hz, 1H), 3.83 (s, 3H), 2.55 (td, J = 13.4, 6.2 Hz, 1H), 2.49 – 2.35 (m, 2H), 1.98 – 1.83 (m, 2H), 1.74–1.55 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 213.0, 200.3, 158.8, 134.1, 131.3, 130.1, 128.0, 127.7, 127.2, 113.7, 63.9, 61.6, 55.2, 39.8, 36.9, 28.3, 20.9. HRMS (EI) Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_3$ ($[\text{M}]^+$): 322.1569. Found: 322.1565.

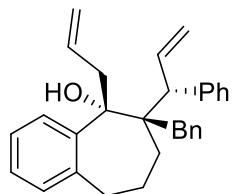
(1R,2R)-2-phenyl-3',4'-dihydro-1'H-spiro[cyclopentane-1,2'-naphthalen]-3-en-1'-one



In a nitrogen-filled dry-box, Grubbs-Hoveyda 2nd generation catalyst (1.16 mg, 0.00184 mmol, 0.0200 equiv), and (R)-2-allyl-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one (28.0 mg, 0.0924 mmol, 1.00 equiv) were dissolved in DCM in a 1-dram vial. The vial was sealed with a cap containing a PTFE-lined silicone-septum, removed from the dry-box, and stirred at 40 °C for

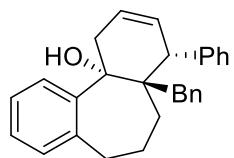
10 h. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to remove the solid. The crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 6:1) to give the product as a colorless oil in 75% yield (19.1 mg). ¹H NMR (600 MHz, Chloroform-d) δ 7.46 – 7.33 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 6.5 Hz, 3H), 6.78 – 6.70 (m, 2H), 6.03 (dd, *J* = 5.5, 2.5 Hz, 1H), 5.56 (dd, *J* = 5.7, 2.5 Hz, 1H), 4.19 (br s, 1H), 3.69 (dd, *J* = 17.1, 2.6 Hz, 1H), 3.56 (ddd, *J* = 17.8, 12.4, 5.3 Hz, 1H), 2.97 (dd, *J* = 17.3, 4.8 Hz, 1H), 2.36 (ddd, *J* = 13.9, 5.3, 2.1 Hz, 1H), 2.21 (td, *J* = 13.1, 5.4 Hz, 1H), 2.07 (dt, *J* = 17.3, 2.3 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 199.3, 141.9, 139.5, 133.4, 132.5, 130.7, 130.1, 128.6, 128.2, 127.54, 127.46, 126.4, 126.1, 57.3, 57.0, 41.9, 35.4, 25.3. HRMS (ESI) Calcd. for C₂₀H₁₈O ([M]⁺): 274.1358. Found: 274.1356.

(5R,6R)-5-allyl-6-benzyl-6-((R)-1-phenylallyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (S1)



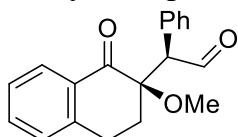
In a nitrogen-filled dry-box, 1.0 M allylmagnesium bromide in THF (0.28 mL, 0.282 mmol, 3.50 equiv) and CeCl₃ (69.5 mg, 0.282 mmol, 3.50 equiv) were added to a 1-dram vial. The mixture was stirred at room temperature for 30 minutes before (R)-6-benzyl-6-((R)-1-phenylallyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (30.0 mg, 0.0820 mmol, 1.00 equiv) in THF (0.30 mL) was added. The vial was sealed with a cap containing a PTFE-lined silicone-septum, removed from the dry-box, and stirred at room temperature for 10 h. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc) to quench the reaction. The crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 3:1) to give the product as a white foam in 92% yield and 9:1 dr. (55.2 mg). ¹H NMR (500 MHz, Chloroform-d) δ 7.51–7.45 (m, 2H), 7.25 (m, 10H), 6.95–6.87 (m, 2H), 6.32 (dt, *J* = 16.9, 9.7 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 4.89 (d, *J* = 16.8 Hz, 1H), 4.73 (d, *J* = 9.7 Hz, 1H), 4.61 (d, *J* = 17.2 Hz, 1H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 9.2 Hz, 1H), 3.15 – 3.02 (m, 2H), 2.89 – 2.79 (m, 1H), 2.65–2.60 (m, 1H), 2.36 – 2.14 (m, 3H), 2.08–2.02 (m, 1H), 1.99 – 1.83 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 144.2, 141.6, 140.5, 138.9, 138.1, 134.7, 132.2, 131.1, 131.0, 128.9, 128.2, 127.7, 127.2, 126.9, 126.1, 125.4, 117.0, 116.5, 83.3, 54.0, 50.5, 39.9, 38.9, 37.4, 34.05, 22.6. HRMS (ESI) Calcd. for C₃₀H₃₂O ([M]⁺): 408.2453. Found: 408.2447.

(7aR,8R,11aR)-7a-benzyl-8-phenyl-5,6,7,7a,8,11-hexahydro-11aH-dibenzo[a,c][7]annulen-11a-ol



In a nitrogen-filled dry-box, Grubbs-Hoveyda 2nd generation catalyst (4.4 mg, 0.00705 mmol, 0.170 equiv), and **S1** (16.7 mg, 0.041 mmol, 1.00 equiv) were dissolved in DCM (0.3 mL) in a 1-dram vial. The vial was sealed with a cap containing a PTFE-lined silicone-septum, removed from the dry-box, and stirred at 40 °C for 10 h. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the solution was filtered through a 0.5 inch plug of silica gel (eluting with EtOAc). The crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 6:1) to give the product as a colorless oil in 62% yield (9.7 mg). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 6.3 Hz, 1H), 7.28 – 7.13 (m, 11H), 7.09 (d, *J* = 7.1 Hz, 2H), 6.16 – 5.98 (m, 1H), 5.92 (d, *J* = 10.0 Hz, 1H), 3.69 – 3.50 (m, 2H), 3.44 – 3.17 (m, 1H), 2.68 – 2.41 (m, 4H), 1.53 – 1.36 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 142.6, 138.3, 131.3, 131.2, 130.3, 127.8, 127.7, 127.4, 126.7, 126.2, 125.9, 125.4, 122.9, 79.4, 48.6, 45.5, 37.2, 37.2, 35.3, 29.6, 21.9. HRMS (EI) Calcd. for C₂₈H₂₈O ([M]⁺): 380.2140. Found: 380.2139.

(R)-2-((R)-2-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-2-phenylacetaldehyde (**S2**)

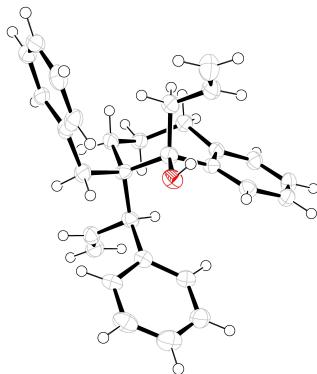


NaIO₄ (137 mg, 0.640 mmol, 3.50 equiv) were dissolved in water (1.50 mL) in a 1-dram vial. 2.5% OsO₄ solution in *t*-BuOH (0.092 mL, 0.00916 mmol, 0.0500 equiv) and (R)-2-methoxy-2-((R)-1-phenylallyl)-3,4-dihydronaphthalen-1(2H)-one (70.0 mg, 0.183 mmol, 1.00 equiv) in ether (1.50 mL) were added to the vial sequentially. After sealing the vial with a cap containing a PTFE-lined silicone-septum, the reaction mixture was stirred at room temperature for 48 hours. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the reaction was quenched by saturated Na₂SO₃ solution. The mixture was poured into a separatory funnel containing EtOAc (3 mL), and the layers were separated. The aqueous layer was extracted by EtOAc (2 x 2 mL), and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column silica gel chromatography (eluting with hexanes:EtOAc, 10:1 to 3:1) to give the product as white solid in 91% yield (63.2 mg). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.90 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.29 (m, 4H), 7.27 – 7.09 (m, 3H), 4.67 (s, 1H), 3.33 (s, 3H), 3.20 (td, *J* = 11.5, 5.7 Hz, 1H), 2.81 (dt, *J* = 17.0, 4.4 Hz, 1H), 2.48 (ddd, *J* = 15.3, 11.1, 5.0 Hz, 1H), 2.09 (dt, *J* = 14.0, 4.3 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 199.3, 194.4, 144.0, 133.9, 131.9, 131.2, 130.9, 128.7, 128.6, 128.3, 128.0, 126.7, 80.5, 57.8, 52.0, 30.0, 24.8. HRMS (ESI) Calcd. for C₁₉H₁₈O₃Na ([M+Na]⁺): 317.1148. Found: 317.1145.

References

1. (a) Ishimaru, T.; Shibata, N.; Horikawa, T.; Yasuda, N.; Nakamura, S.; Toru, T.; Shiro, M., *Angew. Chem., Int. Ed.* **2008**, *47*, 4157; (b) Gao, S.; Tu, Y. Q.; Song, Z.; Wang, A.; Fan, X.; Jiang, Y., *J. Org. Chem.* **2005**, *70*, 6523.
2. Stanley, L. M.; Hartwig, J. F., *Angew. Chem., Int. Ed.* **2009**, *48*, 7841.

Single-crystal X-ray diffraction study of S1



A suitable crystal of **S1** was obtained by slow evaporation of a solution of **S1** in methanol. A colorless plate 0.040 x 0.030 x 0.020 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 67.000° in θ. A total of 110825 reflections were collected covering the indices, $-12 \leq h \leq 11$, $-16 \leq k \leq 16$, $-40 \leq l \leq 39$. 8514 reflections were found to be symmetry independent, with an R_{int} of 0.0806. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P 21 21 21 (No. 19). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at all stereocenters.

Table 1. Crystal data and structure refinement for **S1**.

X-ray ID	S1
Empirical formula	C30 H32 O
Formula weight	408.55
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 10.4745(4) Å a= 90°. b = 13.2976(5) Å b= 90°. c = 33.3082(13) Å g = 90°.
Volume	4639.4(3) Å ³
Z	8
Density (calculated)	1.170 Mg/m ³
Absorption coefficient	0.521 mm ⁻¹
F(000)	1760
Crystal size	0.040 x 0.030 x 0.020 mm ³
Theta range for data collection	2.653 to 68.604°.
Index ranges	-12<=h<=11, -16<=k<=16, -40<=l<=39
Reflections collected	110825
Independent reflections	8514 [R(int) = 0.0806]
Completeness to theta = 67.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.929 and 0.806
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8514 / 0 / 561
Goodness-of-fit on F ²	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0673, wR2 = 0.1792
R indices (all data)	R1 = 0.0712, wR2 = 0.1820
Absolute structure parameter	0.10(14)
Extinction coefficient	n/a
Largest diff. peak and hole	0.351 and -0.315 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **S1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6204(5)	4835(4)	5792(2)	28(1)
C(2)	5474(5)	5819(4)	5689(2)	25(1)
C(3)	5036(5)	5958(4)	5298(2)	30(1)
C(4)	4419(5)	6832(4)	5177(2)	31(1)
C(5)	4237(6)	7600(4)	5450(2)	34(1)
C(6)	4679(5)	7485(4)	5836(2)	30(1)
C(7)	5323(5)	6627(4)	5964(2)	27(1)
C(8)	5852(5)	6649(4)	6391(2)	29(1)
C(9)	5443(5)	5797(4)	6670(2)	28(1)
C(10)	6016(5)	4769(4)	6571(2)	29(1)
C(11)	5644(5)	4247(4)	6172(2)	26(1)
C(12)	7624(5)	5096(4)	5822(2)	29(1)
C(13)	8185(5)	5478(4)	5438(2)	34(1)
C(14)	9140(6)	5049(5)	5248(2)	45(2)
C(15)	6153(5)	3148(4)	6187(2)	31(1)
C(16)	7563(5)	2937(4)	6231(2)	30(1)
C(17)	8214(5)	3073(4)	6588(2)	28(1)
C(18)	9528(6)	2904(4)	6609(2)	34(1)
C(19)	10198(5)	2570(4)	6276(2)	35(1)
C(20)	9550(6)	2395(4)	5924(2)	37(1)
C(21)	8264(6)	2579(4)	5900(2)	34(1)
C(22)	4151(5)	4218(4)	6150(2)	27(1)
C(23)	3518(5)	3744(4)	6516(2)	31(1)
C(24)	2612(5)	4178(4)	6731(2)	35(1)
C(25)	3522(5)	3728(4)	5781(2)	28(1)
C(26)	3444(5)	2678(4)	5724(2)	32(1)
C(27)	2789(6)	2274(5)	5400(2)	40(1)
C(28)	2153(6)	2876(5)	5135(2)	44(2)
C(29)	2160(6)	3921(5)	5188(2)	43(1)
C(30)	2828(5)	4325(4)	5511(2)	34(1)
C(31)	-1092(5)	3338(4)	8272(1)	23(1)

C(32)	-375(5)	2362(4)	8158(2)	28(1)
C(33)	113(5)	2274(4)	7770(2)	30(1)
C(34)	701(6)	1411(5)	7630(2)	39(1)
C(35)	839(6)	598(4)	7882(2)	37(1)
C(36)	330(5)	651(4)	8267(2)	31(1)
C(37)	-285(5)	1514(4)	8410(2)	29(1)
C(38)	-883(5)	1432(4)	8826(2)	30(1)
C(39)	-526(5)	2237(4)	9133(2)	31(1)
C(40)	-1045(5)	3289(4)	9053(1)	24(1)
C(41)	-600(5)	3849(4)	8675(2)	26(1)
C(42)	-2537(5)	3071(4)	8274(2)	28(1)
C(43)	-2988(5)	2642(4)	7884(2)	33(1)
C(44)	-3786(6)	3086(5)	7641(2)	43(1)
C(45)	-1097(5)	4969(4)	8702(2)	27(1)
C(46)	-2508(5)	5182(4)	8709(2)	27(1)
C(47)	-3107(5)	5581(4)	8368(2)	32(1)
C(48)	-4398(6)	5773(4)	8360(2)	36(1)
C(49)	-5158(6)	5568(4)	8696(2)	40(1)
C(50)	-4573(6)	5206(4)	9039(2)	37(1)
C(51)	-3273(5)	5025(4)	9049(2)	30(1)
C(52)	930(5)	3871(4)	8679(2)	26(1)
C(53)	1464(5)	4327(4)	9060(2)	30(1)
C(54)	2287(6)	3863(5)	9296(2)	37(1)
C(55)	1629(4)	4338(4)	8325(1)	23(1)
C(56)	2353(5)	3710(4)	8077(2)	29(1)
C(57)	3036(5)	4092(4)	7758(2)	32(1)
C(58)	3012(5)	5116(4)	7679(2)	32(1)
C(59)	2322(5)	5747(4)	7925(2)	31(1)
C(60)	1642(5)	5374(4)	8249(2)	30(1)
O(1)	6119(4)	4152(3)	5455(1)	31(1)
O(2)	-990(4)	4053(3)	7951(1)	29(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **S1**.

C(1)-O(1)	1.448(6)	C(1)-C(12)	1.530(8)
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C(1)-C(2)	1.554(7)	C(17)-C(18)	1.396(8)
C(1)-C(11)	1.598(7)	C(17)-H(17)	0.9500
C(2)-C(3)	1.395(7)	C(18)-C(19)	1.385(8)
C(2)-C(7)	1.421(7)	C(18)-H(18)	0.9500
C(3)-C(4)	1.389(7)	C(19)-C(20)	1.376(8)
C(3)-H(3)	0.9500	C(19)-H(19)	0.9500
C(4)-C(5)	1.379(8)	C(20)-C(21)	1.371(8)
C(4)-H(4)	0.9500	C(20)-H(20)	0.9500
C(5)-C(6)	1.376(7)	C(21)-H(21)	0.9500
C(5)-H(5)	0.9500	C(22)-C(23)	1.526(7)
C(6)-C(7)	1.393(7)	C(22)-C(25)	1.537(7)
C(6)-H(6)	0.9500	C(22)-H(22)	1.0000
C(7)-C(8)	1.525(7)	C(23)-C(24)	1.322(8)
C(8)-C(9)	1.525(7)	C(23)-H(23)	0.9500
C(8)-H(8A)	0.9900	C(24)-H(24A)	0.9500
C(8)-H(8B)	0.9900	C(24)-H(24B)	0.9500
C(9)-C(10)	1.530(7)	C(25)-C(30)	1.404(7)
C(9)-H(9A)	0.9900	C(25)-C(26)	1.412(7)
C(9)-H(9B)	0.9900	C(26)-C(27)	1.387(8)
C(10)-C(11)	1.548(7)	C(26)-H(26)	0.9500
C(10)-H(10A)	0.9900	C(27)-C(28)	1.366(9)
C(10)-H(10B)	0.9900	C(27)-H(27)	0.9500
C(11)-C(15)	1.556(7)	C(28)-C(29)	1.400(9)
C(11)-C(22)	1.566(7)	C(28)-H(28)	0.9500
C(12)-C(13)	1.496(7)	C(29)-C(30)	1.391(8)
C(12)-H(12A)	0.9900	C(29)-H(29)	0.9500
C(12)-H(12B)	0.9900	C(30)-H(30)	0.9500
C(13)-C(14)	1.313(8)	C(31)-O(2)	1.436(6)
C(13)-H(13)	0.9500	C(31)-C(32)	1.547(7)
C(14)-H(14A)	0.9500	C(31)-C(42)	1.555(7)
C(14)-H(14B)	0.9500	C(31)-C(41)	1.589(7)
C(15)-C(16)	1.511(8)	C(32)-C(33)	1.395(7)
C(15)-H(15A)	0.9900	C(32)-C(37)	1.410(7)
C(15)-H(15B)	0.9900	C(33)-C(34)	1.383(8)
C(16)-C(17)	1.383(7)	C(33)-H(33)	0.9500
C(16)-C(21)	1.409(8)	C(34)-C(35)	1.377(8)

C(34)-H(34)	0.9500	C(47)-C(48)	1.376(8)
C(35)-C(36)	1.389(8)	C(47)-H(47)	0.9500
C(35)-H(35)	0.9500	C(48)-C(49)	1.402(9)
C(36)-C(37)	1.400(8)	C(48)-H(48)	0.9500
C(36)-H(36)	0.9500	C(49)-C(50)	1.382(8)
C(37)-C(38)	1.523(7)	C(49)-H(49)	0.9500
C(38)-C(39)	1.527(7)	C(50)-C(51)	1.382(8)
C(38)-H(38A)	0.9900	C(50)-H(50)	0.9500
C(38)-H(38B)	0.9900	C(51)-H(51)	0.9500
C(39)-C(40)	1.525(7)	C(52)-C(53)	1.513(7)
C(39)-H(39A)	0.9900	C(52)-C(55)	1.523(7)
C(39)-H(39B)	0.9900	C(52)-H(52)	1.0000
C(40)-C(41)	1.535(7)	C(53)-C(54)	1.320(8)
C(40)-H(40A)	0.9900	C(53)-H(53)	0.9500
C(40)-H(40B)	0.9900	C(54)-H(54A)	0.9500
C(41)-C(45)	1.580(7)	C(54)-H(54B)	0.9500
C(41)-C(52)	1.602(7)	C(55)-C(56)	1.397(7)
C(42)-C(43)	1.496(7)	C(55)-C(60)	1.400(7)
C(42)-H(42A)	0.9900	C(56)-C(57)	1.379(7)
C(42)-H(42B)	0.9900	C(56)-H(56)	0.9500
C(43)-C(44)	1.305(8)	C(57)-C(58)	1.386(8)
C(43)-H(43)	0.9500	C(57)-H(57)	0.9500
C(44)-H(44A)	0.9500	C(58)-C(59)	1.379(8)
C(44)-H(44B)	0.9500	C(58)-H(58)	0.9500
C(45)-C(46)	1.504(8)	C(59)-C(60)	1.384(7)
C(45)-H(45A)	0.9900	C(59)-H(59)	0.9500
C(45)-H(45B)	0.9900	C(60)-H(60)	0.9500
C(46)-C(47)	1.401(7)	O(1)-H(1)	0.8400
C(46)-C(51)	1.403(7)	O(2)-H(2)	0.8400
O(1)-C(1)-C(12)	104.6(4)	C(3)-C(2)-C(7)	117.8(5)
O(1)-C(1)-C(2)	109.1(4)	C(3)-C(2)-C(1)	118.7(4)
C(12)-C(1)-C(2)	107.6(4)	C(7)-C(2)-C(1)	123.3(4)
O(1)-C(1)-C(11)	106.5(4)	C(4)-C(3)-C(2)	122.3(5)
C(12)-C(1)-C(11)	114.7(4)	C(4)-C(3)-H(3)	118.8
C(2)-C(1)-C(11)	114.0(4)	C(2)-C(3)-H(3)	118.8

C(5)-C(4)-C(3)	119.5(5)	C(13)-C(12)-C(1)	113.8(4)
C(5)-C(4)-H(4)	120.3	C(13)-C(12)-H(12A)	108.8
C(3)-C(4)-H(4)	120.3	C(1)-C(12)-H(12A)	108.8
C(6)-C(5)-C(4)	119.2(5)	C(13)-C(12)-H(12B)	108.8
C(6)-C(5)-H(5)	120.4	C(1)-C(12)-H(12B)	108.8
C(4)-C(5)-H(5)	120.4	H(12A)-C(12)-H(12B)	107.7
C(5)-C(6)-C(7)	122.7(5)	C(14)-C(13)-C(12)	124.3(5)
C(5)-C(6)-H(6)	118.6	C(14)-C(13)-H(13)	117.8
C(7)-C(6)-H(6)	118.6	C(12)-C(13)-H(13)	117.8
C(6)-C(7)-C(2)	118.4(5)	C(13)-C(14)-H(14A)	120.0
C(6)-C(7)-C(8)	116.5(4)	C(13)-C(14)-H(14B)	120.0
C(2)-C(7)-C(8)	125.0(4)	H(14A)-C(14)-H(14B)	120.0
C(7)-C(8)-C(9)	116.8(4)	C(16)-C(15)-C(11)	120.8(4)
C(7)-C(8)-H(8A)	108.1	C(16)-C(15)-H(15A)	107.1
C(9)-C(8)-H(8A)	108.1	C(11)-C(15)-H(15A)	107.1
C(7)-C(8)-H(8B)	108.1	C(16)-C(15)-H(15B)	107.1
C(9)-C(8)-H(8B)	108.1	C(11)-C(15)-H(15B)	107.1
H(8A)-C(8)-H(8B)	107.3	H(15A)-C(15)-H(15B)	106.8
C(8)-C(9)-C(10)	115.0(4)	C(17)-C(16)-C(21)	117.5(5)
C(8)-C(9)-H(9A)	108.5	C(17)-C(16)-C(15)	122.7(5)
C(10)-C(9)-H(9A)	108.5	C(21)-C(16)-C(15)	119.8(5)
C(8)-C(9)-H(9B)	108.5	C(16)-C(17)-C(18)	120.5(5)
C(10)-C(9)-H(9B)	108.5	C(16)-C(17)-H(17)	119.8
H(9A)-C(9)-H(9B)	107.5	C(18)-C(17)-H(17)	119.8
C(9)-C(10)-C(11)	119.1(4)	C(19)-C(18)-C(17)	120.8(5)
C(9)-C(10)-H(10A)	107.5	C(19)-C(18)-H(18)	119.6
C(11)-C(10)-H(10A)	107.5	C(17)-C(18)-H(18)	119.6
C(9)-C(10)-H(10B)	107.5	C(20)-C(19)-C(18)	119.1(5)
C(11)-C(10)-H(10B)	107.5	C(20)-C(19)-H(19)	120.4
H(10A)-C(10)-H(10B)	107.0	C(18)-C(19)-H(19)	120.4
C(10)-C(11)-C(15)	107.8(4)	C(21)-C(20)-C(19)	120.3(5)
C(10)-C(11)-C(22)	107.7(4)	C(21)-C(20)-H(20)	119.8
C(15)-C(11)-C(22)	108.7(4)	C(19)-C(20)-H(20)	119.8
C(10)-C(11)-C(1)	111.5(4)	C(20)-C(21)-C(16)	121.7(5)
C(15)-C(11)-C(1)	111.1(4)	C(20)-C(21)-H(21)	119.1
C(22)-C(11)-C(1)	110.0(4)	C(16)-C(21)-H(21)	119.1

C(23)-C(22)-C(25)	106.1(4)	C(33)-C(32)-C(37)	117.5(5)
C(23)-C(22)-C(11)	114.0(4)	C(33)-C(32)-C(31)	118.4(4)
C(25)-C(22)-C(11)	118.5(4)	C(37)-C(32)-C(31)	123.8(4)
C(23)-C(22)-H(22)	105.8	C(34)-C(33)-C(32)	123.0(5)
C(25)-C(22)-H(22)	105.8	C(34)-C(33)-H(33)	118.5
C(11)-C(22)-H(22)	105.8	C(32)-C(33)-H(33)	118.5
C(24)-C(23)-C(22)	124.4(5)	C(35)-C(34)-C(33)	119.5(5)
C(24)-C(23)-H(23)	117.8	C(35)-C(34)-H(34)	120.3
C(22)-C(23)-H(23)	117.8	C(33)-C(34)-H(34)	120.3
C(23)-C(24)-H(24A)	120.0	C(34)-C(35)-C(36)	118.9(5)
C(23)-C(24)-H(24B)	120.0	C(34)-C(35)-H(35)	120.5
H(24A)-C(24)-H(24B)	120.0	C(36)-C(35)-H(35)	120.5
C(30)-C(25)-C(26)	116.2(5)	C(35)-C(36)-C(37)	122.2(5)
C(30)-C(25)-C(22)	119.7(5)	C(35)-C(36)-H(36)	118.9
C(26)-C(25)-C(22)	123.5(5)	C(37)-C(36)-H(36)	118.9
C(27)-C(26)-C(25)	121.1(5)	C(36)-C(37)-C(32)	118.9(5)
C(27)-C(26)-H(26)	119.4	C(36)-C(37)-C(38)	116.2(5)
C(25)-C(26)-H(26)	119.4	C(32)-C(37)-C(38)	124.9(5)
C(28)-C(27)-C(26)	121.2(6)	C(37)-C(38)-C(39)	117.3(4)
C(28)-C(27)-H(27)	119.4	C(37)-C(38)-H(38A)	108.0
C(26)-C(27)-H(27)	119.4	C(39)-C(38)-H(38A)	108.0
C(27)-C(28)-C(29)	119.8(6)	C(37)-C(38)-H(38B)	108.0
C(27)-C(28)-H(28)	120.1	C(39)-C(38)-H(38B)	108.0
C(29)-C(28)-H(28)	120.1	H(38A)-C(38)-H(38B)	107.2
C(30)-C(29)-C(28)	119.0(6)	C(40)-C(39)-C(38)	116.0(4)
C(30)-C(29)-H(29)	120.5	C(40)-C(39)-H(39A)	108.3
C(28)-C(29)-H(29)	120.5	C(38)-C(39)-H(39A)	108.3
C(29)-C(30)-C(25)	122.5(6)	C(40)-C(39)-H(39B)	108.3
C(29)-C(30)-H(30)	118.7	C(38)-C(39)-H(39B)	108.3
C(25)-C(30)-H(30)	118.7	H(39A)-C(39)-H(39B)	107.4
O(2)-C(31)-C(32)	109.6(4)	C(39)-C(40)-C(41)	118.7(4)
O(2)-C(31)-C(42)	103.2(4)	C(39)-C(40)-H(40A)	107.6
C(32)-C(31)-C(42)	106.4(4)	C(41)-C(40)-H(40A)	107.6
O(2)-C(31)-C(41)	108.8(4)	C(39)-C(40)-H(40B)	107.6
C(32)-C(31)-C(41)	114.1(4)	C(41)-C(40)-H(40B)	107.6
C(42)-C(31)-C(41)	114.2(4)	H(40A)-C(40)-H(40B)	107.1

C(40)-C(41)-C(45)	108.0(4)	C(49)-C(50)-C(51)	121.2(6)
C(40)-C(41)-C(31)	112.7(4)	C(49)-C(50)-H(50)	119.4
C(45)-C(41)-C(31)	110.2(4)	C(51)-C(50)-H(50)	119.4
C(40)-C(41)-C(52)	107.8(4)	C(50)-C(51)-C(46)	121.2(5)
C(45)-C(41)-C(52)	108.2(4)	C(50)-C(51)-H(51)	119.4
C(31)-C(41)-C(52)	109.9(4)	C(46)-C(51)-H(51)	119.4
C(43)-C(42)-C(31)	113.0(4)	C(53)-C(52)-C(55)	107.9(4)
C(43)-C(42)-H(42A)	109.0	C(53)-C(52)-C(41)	112.7(4)
C(31)-C(42)-H(42A)	109.0	C(55)-C(52)-C(41)	118.8(4)
C(43)-C(42)-H(42B)	109.0	C(53)-C(52)-H(52)	105.5
C(31)-C(42)-H(42B)	109.0	C(55)-C(52)-H(52)	105.5
H(42A)-C(42)-H(42B)	107.8	C(41)-C(52)-H(52)	105.5
C(44)-C(43)-C(42)	124.6(5)	C(54)-C(53)-C(52)	123.6(5)
C(44)-C(43)-H(43)	117.7	C(54)-C(53)-H(53)	118.2
C(42)-C(43)-H(43)	117.7	C(52)-C(53)-H(53)	118.2
C(43)-C(44)-H(44A)	120.0	C(53)-C(54)-H(54A)	120.0
C(43)-C(44)-H(44B)	120.0	C(53)-C(54)-H(54B)	120.0
H(44A)-C(44)-H(44B)	120.0	H(54A)-C(54)-H(54B)	120.0
C(46)-C(45)-C(41)	120.2(4)	C(56)-C(55)-C(60)	118.4(5)
C(46)-C(45)-H(45A)	107.3	C(56)-C(55)-C(52)	118.3(4)
C(41)-C(45)-H(45A)	107.3	C(60)-C(55)-C(52)	123.1(4)
C(46)-C(45)-H(45B)	107.3	C(57)-C(56)-C(55)	121.1(5)
C(41)-C(45)-H(45B)	107.3	C(57)-C(56)-H(56)	119.5
H(45A)-C(45)-H(45B)	106.9	C(55)-C(56)-H(56)	119.5
C(47)-C(46)-C(51)	117.0(5)	C(56)-C(57)-C(58)	120.0(5)
C(47)-C(46)-C(45)	120.0(5)	C(56)-C(57)-H(57)	120.0
C(51)-C(46)-C(45)	123.0(5)	C(58)-C(57)-H(57)	120.0
C(48)-C(47)-C(46)	121.8(5)	C(59)-C(58)-C(57)	119.6(5)
C(48)-C(47)-H(47)	119.1	C(59)-C(58)-H(58)	120.2
C(46)-C(47)-H(47)	119.1	C(57)-C(58)-H(58)	120.2
C(47)-C(48)-C(49)	120.4(6)	C(58)-C(59)-C(60)	121.0(5)
C(47)-C(48)-H(48)	119.8	C(58)-C(59)-H(59)	119.5
C(49)-C(48)-H(48)	119.8	C(60)-C(59)-H(59)	119.5
C(50)-C(49)-C(48)	118.4(6)	C(59)-C(60)-C(55)	119.9(5)
C(50)-C(49)-H(49)	120.8	C(59)-C(60)-H(60)	120.1
C(48)-C(49)-H(49)	120.8	C(55)-C(60)-H(60)	120.1

C(1)-O(1)-H(1)	109.5
C(31)-O(2)-H(2)	109.5

Symmetry transformations used to generate equivalent atoms

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **S1**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^* a^* U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(1)	35(3)	20(2)	29(2)	-6(2)	-3(2)	-3(2)
C(2)	22(2)	24(2)	30(2)	-3(2)	-1(2)	0(2)
C(3)	34(3)	28(3)	27(2)	-2(2)	1(2)	-4(2)
C(4)	28(3)	34(3)	31(3)	6(2)	-1(2)	1(2)
C(5)	40(3)	27(3)	34(3)	6(2)	-1(2)	3(2)
C(6)	32(3)	25(3)	34(3)	1(2)	3(2)	2(2)
C(7)	31(3)	20(2)	29(2)	-1(2)	-2(2)	-3(2)
C(8)	34(3)	23(2)	31(3)	-5(2)	-4(2)	1(2)
C(9)	31(3)	26(3)	27(2)	-3(2)	-5(2)	-2(2)
C(10)	36(3)	22(2)	29(3)	-1(2)	-5(2)	-5(2)
C(11)	22(2)	23(2)	32(3)	-3(2)	-3(2)	3(2)
C(12)	34(3)	21(2)	33(3)	-3(2)	-1(2)	1(2)
C(13)	33(3)	28(3)	39(3)	3(2)	2(2)	3(2)
C(14)	48(4)	45(4)	42(3)	9(3)	12(3)	13(3)
C(15)	35(3)	20(2)	37(3)	-1(2)	-5(2)	2(2)
C(16)	38(3)	19(2)	32(3)	2(2)	-4(2)	1(2)
C(17)	31(3)	21(2)	32(3)	2(2)	-5(2)	1(2)
C(18)	39(3)	25(3)	37(3)	2(2)	-8(2)	-5(2)
C(19)	25(3)	26(3)	54(3)	7(2)	2(2)	2(2)
C(20)	47(4)	27(3)	38(3)	4(2)	8(3)	6(3)
C(21)	40(3)	26(3)	34(3)	-2(2)	-6(2)	7(2)
C(22)	29(3)	21(2)	31(2)	-3(2)	-1(2)	-2(2)
C(23)	37(3)	28(3)	29(3)	0(2)	-1(2)	-2(2)
C(24)	32(3)	37(3)	35(3)	0(2)	-4(2)	-1(2)
C(25)	26(3)	27(3)	30(3)	-3(2)	4(2)	0(2)
C(26)	27(3)	30(3)	38(3)	-4(2)	0(2)	-8(2)

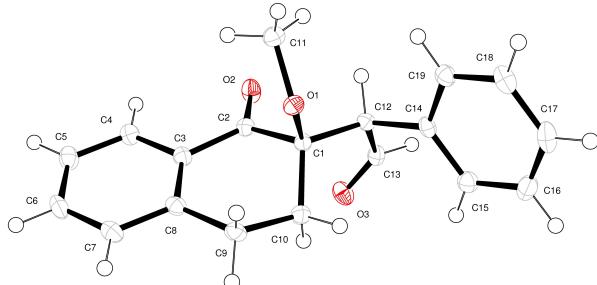
C(27)	44(4)	37(3)	40(3)	-13(3)	9(3)	-11(3)
C(28)	44(4)	57(4)	30(3)	-10(3)	4(3)	-11(3)
C(29)	42(3)	56(4)	30(3)	7(3)	-3(3)	-13(3)
C(30)	26(3)	37(3)	39(3)	2(2)	-1(2)	-4(2)
C(31)	22(2)	22(2)	26(2)	1(2)	0(2)	1(2)
C(32)	31(3)	25(2)	28(2)	-4(2)	-5(2)	0(2)
C(33)	28(3)	32(3)	31(3)	-2(2)	-1(2)	2(2)
C(34)	43(3)	43(3)	32(3)	-13(2)	4(2)	4(3)
C(35)	34(3)	37(3)	40(3)	-11(2)	-8(2)	7(3)
C(36)	28(3)	28(3)	36(3)	-5(2)	-7(2)	-1(2)
C(37)	31(3)	26(3)	31(3)	-3(2)	-4(2)	-5(2)
C(38)	34(3)	22(2)	35(3)	1(2)	0(2)	2(2)
C(39)	38(3)	28(3)	27(3)	3(2)	1(2)	-2(2)
C(40)	24(2)	24(2)	25(2)	1(2)	0(2)	-1(2)
C(41)	35(3)	19(2)	26(2)	0(2)	2(2)	3(2)
C(42)	32(3)	23(2)	29(2)	-1(2)	-1(2)	0(2)
C(43)	33(3)	31(3)	35(3)	-5(2)	0(2)	-1(2)
C(44)	38(3)	51(4)	38(3)	-7(3)	-8(3)	2(3)
C(45)	31(3)	21(2)	30(2)	-1(2)	0(2)	-2(2)
C(46)	30(3)	18(2)	34(3)	-3(2)	1(2)	1(2)
C(47)	36(3)	26(3)	35(3)	2(2)	-4(2)	-1(2)
C(48)	40(3)	26(3)	44(3)	-1(2)	-10(3)	2(2)
C(49)	33(3)	26(3)	60(4)	-6(3)	-5(3)	-5(2)
C(50)	36(3)	26(3)	47(3)	0(2)	7(3)	1(2)
C(51)	33(3)	20(2)	38(3)	-1(2)	2(2)	2(2)
C(52)	26(3)	21(2)	29(2)	1(2)	-1(2)	4(2)
C(53)	30(3)	30(3)	30(3)	-2(2)	3(2)	-1(2)
C(54)	41(3)	42(3)	30(3)	0(2)	-1(2)	-10(3)
C(55)	15(2)	25(2)	29(2)	1(2)	-3(2)	-1(2)
C(56)	31(3)	24(2)	33(3)	-2(2)	-3(2)	2(2)
C(57)	30(3)	34(3)	32(3)	0(2)	1(2)	1(2)
C(58)	34(3)	35(3)	28(3)	3(2)	5(2)	0(2)
C(59)	31(3)	31(3)	32(3)	2(2)	-2(2)	-6(2)
C(60)	36(3)	24(3)	29(3)	-2(2)	-4(2)	2(2)
O(1)	37(2)	27(2)	28(2)	-7(2)	2(2)	-4(2)
O(2)	31(2)	28(2)	28(2)	6(2)	1(2)	-1(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **S1**.

	x	y	z	U(eq)
H(3)	5164	5437	5107	35
H(4)	4124	6901	4909	37
H(5)	3813	8200	5372	41
H(6)	4538	8013	6023	37
H(8A)	5597	7294	6516	35
H(8B)	6796	6645	6374	35
H(9A)	4501	5742	6661	34
H(9B)	5685	5978	6948	34
H(10A)	5791	4306	6792	35
H(10B)	6957	4841	6573	35
H(12A)	7740	5614	6033	35
H(12B)	8100	4489	5906	35
H(13)	7827	6069	5324	40
H(14A)	9520	4457	5354	54
H(14B)	9451	5331	5005	54
H(15A)	5716	2809	6414	37
H(15B)	5864	2810	5939	37
H(17)	7763	3282	6821	33
H(18)	9967	3020	6854	40
H(19)	11094	2464	6291	42
H(20)	9995	2145	5696	45
H(21)	7835	2462	5653	40
H(22)	3869	4936	6147	32
H(23)	3793	3093	6595	37
H(24A)	2314	4830	6661	42
H(24B)	2260	3839	6957	42
H(26)	3846	2240	5910	38
H(27)	2784	1566	5361	48
H(28)	1708	2588	4915	53
H(29)	1715	4346	5007	51
H(30)	2814	5033	5550	40

H(33)	37	2832	7593	37
H(34)	1008	1380	7362	47
H(35)	1274	11	7795	45
H(36)	403	83	8439	37
H(38A)	-651	769	8939	36
H(38B)	-1822	1441	8793	36
H(39A)	-834	2016	9400	37
H(39B)	417	2277	9147	37
H(40A)	-831	3713	9287	29
H(40B)	-1988	3241	9041	29
H(42A)	-2703	2578	8491	34
H(42B)	-3035	3685	8335	34
H(43)	-2671	2000	7808	40
H(44A)	-4122	3728	7708	51
H(44B)	-4030	2768	7398	51
H(45A)	-728	5267	8949	33
H(45B)	-731	5340	8472	33
H(47)	-2608	5723	8137	38
H(48)	-4776	6046	8124	44
H(49)	-6054	5676	8689	48
H(50)	-5072	5078	9271	44
H(51)	-2892	4791	9290	36
H(52)	1201	3150	8684	31
H(53)	1193	4984	9133	36
H(54A)	2575	3206	9231	45
H(54B)	2591	4187	9532	45
H(56)	2375	3008	8130	35
H(57)	3522	3655	7592	38
H(58)	3469	5381	7456	39
H(59)	2314	6449	7872	38
H(60)	1184	5819	8419	36
H(1)	6645	4324	5278	46
H(2)	-251	4299	7949	44

Single-crystal X-ray diffraction study of S2



A suitable crystal of **S2** was obtained by diffusing pentane into a solution of **S2** in ether. A colorless prism $0.120 \times 0.100 \times 0.020$ mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at $100(2)$ K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 2.0° . Data collection was 100.0% complete to 67.000° in θ . A total of 19001 reflections were collected covering the indices, $-12 \leq h \leq 11$, $-7 \leq k \leq 7$, $-13 \leq l \leq 13$. 2652 reflections were found to be symmetry independent, with an R_{int} of 0.0183. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P\bar{1}1$ (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2013. Absolute stereochemistry was unambiguously determined to be *R* at C1 and C12, respectively.

Table 1. Crystal data and structure refinement for **S2**.

Empirical formula	C19 H18 O3	
Formula weight	294.33	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	$a = 10.4253(3)$ Å	$\alpha = 90^\circ$.
	$b = 6.4492(2)$ Å	$\beta = 110.0110(10)^\circ$.
	$c = 11.5276(4)$ Å	$\gamma = 90^\circ$.
Volume	$728.26(4)$ Å ³	
Z	2	
Density (calculated)	1.342 Mg/m ³	
Absorption coefficient	0.723 mm ⁻¹	
F(000)	312	
Crystal size	0.120 x 0.100 x 0.020 mm ³	
Crystal color/habit	colorless prism	
Theta range for data collection	4.081 to 68.328°.	
Index ranges	-12≤h≤11, -7≤k≤7, -13≤l≤13	
Reflections collected	19001	
Independent reflections	2652 [R(int) = 0.0183]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.837	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2652 / 1 / 200	
Goodness-of-fit on F ²	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0889	
R indices (all data)	R1 = 0.0341, wR2 = 0.0893	
Absolute structure parameter	-0.03(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.215 and -0.183 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **S2**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	1024(2)	3662(3)	7610(2)	14(1)
C(2)	2063(2)	5221(3)	8424(2)	15(1)
C(3)	3483(2)	5064(3)	8409(2)	16(1)
C(4)	4393(2)	6673(4)	8942(2)	18(1)
C(5)	5704(2)	6643(4)	8899(2)	21(1)
C(6)	6112(2)	4958(4)	8354(2)	22(1)
C(7)	5228(2)	3347(4)	7845(2)	21(1)
C(8)	3888(2)	3370(4)	7852(2)	17(1)
C(9)	2916(2)	1633(3)	7262(2)	19(1)
C(10)	1684(2)	1535(3)	7691(2)	18(1)
C(11)	468(2)	6443(4)	6075(2)	21(1)
C(12)	-300(2)	3664(3)	7935(2)	15(1)
C(13)	-84(2)	3049(3)	9256(2)	18(1)
C(14)	-1446(2)	2373(3)	7046(2)	16(1)
C(15)	-1687(2)	345(4)	7337(2)	20(1)
C(16)	-2733(2)	-817(4)	6518(2)	24(1)
C(17)	-3528(2)	14(4)	5392(2)	25(1)
C(18)	-3294(2)	2025(4)	5096(2)	24(1)
C(19)	-2270(2)	3205(4)	5919(2)	19(1)
O(1)	724(1)	4292(2)	6349(1)	16(1)
O(2)	1720(2)	6587(3)	8981(1)	22(1)
O(3)	991(2)	2562(3)	10022(1)	23(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **S2**.

C(1)-O(1)	1.437(2)	C(16)-H(16)	0.9500
C(1)-C(10)	1.524(3)	C(17)-C(18)	1.384(4)
C(1)-C(2)	1.539(3)	C(17)-H(17)	0.9500
C(1)-C(12)	1.549(3)	C(18)-C(19)	1.387(3)
C(2)-O(2)	1.214(3)	C(18)-H(18)	0.9500
C(2)-C(3)	1.490(3)	C(19)-H(19)	0.9500
C(3)-C(4)	1.398(3)	O(1)-C(1)-C(10)	104.72(16)
C(3)-C(8)	1.403(3)	O(1)-C(1)-C(2)	107.25(16)
C(4)-C(5)	1.384(3)	C(10)-C(1)-C(2)	109.99(16)
C(4)-H(4)	0.9500	O(1)-C(1)-C(12)	109.96(15)
C(5)-C(6)	1.393(3)	C(10)-C(1)-C(12)	114.01(16)
C(5)-H(5)	0.9500	C(2)-C(1)-C(12)	110.56(16)
C(6)-C(7)	1.380(3)	O(2)-C(2)-C(3)	121.98(19)
C(6)-H(6)	0.9500	O(2)-C(2)-C(1)	121.55(18)
C(7)-C(8)	1.400(3)	C(3)-C(2)-C(1)	116.29(17)
C(7)-H(7)	0.9500	C(4)-C(3)-C(8)	120.93(19)
C(8)-C(9)	1.507(3)	C(4)-C(3)-C(2)	118.14(18)
C(9)-C(10)	1.528(3)	C(8)-C(3)-C(2)	120.92(18)
C(9)-H(9A)	0.9900	C(5)-C(4)-C(3)	120.2(2)
C(9)-H(9B)	0.9900	C(5)-C(4)-H(4)	119.9
C(10)-H(10A)	0.9900	C(3)-C(4)-H(4)	119.9
C(10)-H(10B)	0.9900	C(4)-C(5)-C(6)	119.0(2)
C(11)-O(1)	1.427(3)	C(4)-C(5)-H(5)	120.5
C(11)-H(11A)	0.9800	C(6)-C(5)-H(5)	120.5
C(11)-H(11B)	0.9800	C(7)-C(6)-C(5)	121.10(19)
C(11)-H(11C)	0.9800	C(7)-C(6)-H(6)	119.5
C(12)-C(13)	1.514(3)	C(5)-C(6)-H(6)	119.5
C(12)-C(14)	1.527(3)	C(6)-C(7)-C(8)	120.8(2)
C(12)-H(12)	1.0000	C(6)-C(7)-H(7)	119.6
C(13)-O(3)	1.207(3)	C(8)-C(7)-H(7)	119.6
C(13)-H(13)	0.9500	C(7)-C(8)-C(3)	117.9(2)
C(14)-C(15)	1.394(3)	C(7)-C(8)-C(9)	120.49(19)
C(14)-C(19)	1.397(3)	C(3)-C(8)-C(9)	121.62(18)
C(15)-C(16)	1.392(3)	C(8)-C(9)-C(10)	113.24(17)
C(15)-H(15)	0.9500	C(8)-C(9)-H(9A)	108.9
C(16)-C(17)	1.386(3)	C(10)-C(9)-H(9A)	108.9

C(8)-C(9)-H(9B)	108.9	O(3)-C(13)-H(13)	117.1
C(10)-C(9)-H(9B)	108.9	C(12)-C(13)-H(13)	117.1
H(9A)-C(9)-H(9B)	107.7	C(15)-C(14)-C(19)	118.7(2)
C(1)-C(10)-C(9)	110.80(17)	C(15)-C(14)-C(12)	120.95(19)
C(1)-C(10)-H(10A)	109.5	C(19)-C(14)-C(12)	120.38(19)
C(9)-C(10)-H(10A)	109.5	C(16)-C(15)-C(14)	120.4(2)
C(1)-C(10)-H(10B)	109.5	C(16)-C(15)-H(15)	119.8
C(9)-C(10)-H(10B)	109.5	C(14)-C(15)-H(15)	119.8
H(10A)-C(10)-H(10B)	108.1	C(17)-C(16)-C(15)	120.4(2)
O(1)-C(11)-H(11A)	109.5	C(17)-C(16)-H(16)	119.8
O(1)-C(11)-H(11B)	109.5	C(15)-C(16)-H(16)	119.8
H(11A)-C(11)-H(11B)	109.5	C(18)-C(17)-C(16)	119.6(2)
O(1)-C(11)-H(11C)	109.5	C(18)-C(17)-H(17)	120.2
H(11A)-C(11)-H(11C)	109.5	C(16)-C(17)-H(17)	120.2
H(11B)-C(11)-H(11C)	109.5	C(17)-C(18)-C(19)	120.3(2)
C(13)-C(12)-C(14)	110.17(17)	C(17)-C(18)-H(18)	119.9
C(13)-C(12)-C(1)	113.90(16)	C(19)-C(18)-H(18)	119.9
C(14)-C(12)-C(1)	113.23(16)	C(18)-C(19)-C(14)	120.7(2)
C(13)-C(12)-H(12)	106.3	C(18)-C(19)-H(19)	119.7
C(14)-C(12)-H(12)	106.3	C(14)-C(19)-H(19)	119.7
C(1)-C(12)-H(12)	106.3	C(11)-O(1)-C(1)	117.23(16)
O(3)-C(13)-C(12)	125.80(19)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **S2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	14(1)	15(1)	14(1)	1(1)	5(1)	0(1)
C(2)	16(1)	16(1)	13(1)	1(1)	6(1)	0(1)
C(3)	15(1)	20(1)	14(1)	2(1)	4(1)	1(1)
C(4)	18(1)	21(1)	17(1)	-1(1)	6(1)	0(1)
C(5)	17(1)	27(1)	18(1)	0(1)	3(1)	-3(1)
C(6)	13(1)	31(1)	22(1)	4(1)	7(1)	2(1)

C(7)	18(1)	25(1)	19(1)	2(1)	7(1)	6(1)
C(8)	17(1)	20(1)	15(1)	2(1)	5(1)	3(1)
C(9)	19(1)	17(1)	22(1)	-1(1)	8(1)	4(1)
C(10)	18(1)	16(1)	20(1)	-1(1)	7(1)	0(1)
C(11)	21(1)	19(1)	23(1)	5(1)	9(1)	2(1)
C(12)	15(1)	15(1)	16(1)	0(1)	6(1)	2(1)
C(13)	17(1)	19(1)	19(1)	-2(1)	8(1)	-3(1)
C(14)	12(1)	20(1)	17(1)	-3(1)	7(1)	1(1)
C(15)	19(1)	21(1)	22(1)	2(1)	8(1)	1(1)
C(16)	24(1)	20(1)	32(1)	-4(1)	14(1)	-5(1)
C(17)	18(1)	34(1)	26(1)	-12(1)	9(1)	-8(1)
C(18)	16(1)	36(1)	18(1)	-1(1)	5(1)	0(1)
C(19)	17(1)	23(1)	18(1)	2(1)	8(1)	1(1)
O(1)	19(1)	16(1)	15(1)	1(1)	7(1)	0(1)
O(2)	20(1)	23(1)	27(1)	-9(1)	12(1)	-3(1)
O(3)	18(1)	33(1)	17(1)	1(1)	4(1)	2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **S2**.

	x	y	z	U(eq)
H(4)	4111	7790	9335	22
H(5)	6316	7755	9237	26
H(6)	7015	4917	8332	26
H(7)	5532	2208	7485	25
H(9A)	3414	299	7457	23
H(9B)	2590	1812	6355	23
H(10A)	1008	540	7170	21
H(10B)	1978	1034	8555	21
H(11A)	-189	6950	6446	31
H(11B)	95	6636	5179	31
H(11C)	1324	7220	6414	31
H(12)	-633	5130	7844	19
H(13)	-864	3045	9504	21
H(15)	-1133	-247	8098	24
H(16)	-2903	-2187	6732	29
H(17)	-4230	-792	4828	30
H(18)	-3835	2600	4325	28
H(19)	-2129	4593	5714	23

8.060
8.057
8.044
8.041

7.514
7.511
7.499
7.496
7.484
7.481
7.367
7.352
7.337
7.308
7.303
7.294
7.290
7.282
7.278
7.263
7.251
7.237
7.231
7.225
7.222
7.164
7.160
7.147
7.147
6.309
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6.255
6.237
5.168
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5.135
5.132
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3.015
3.003
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2.352
2.343
2.335
2.325
1.979
1.968
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dr 11:1

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2.67
2.05
2.05

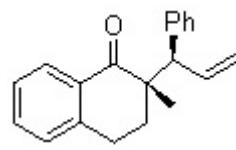
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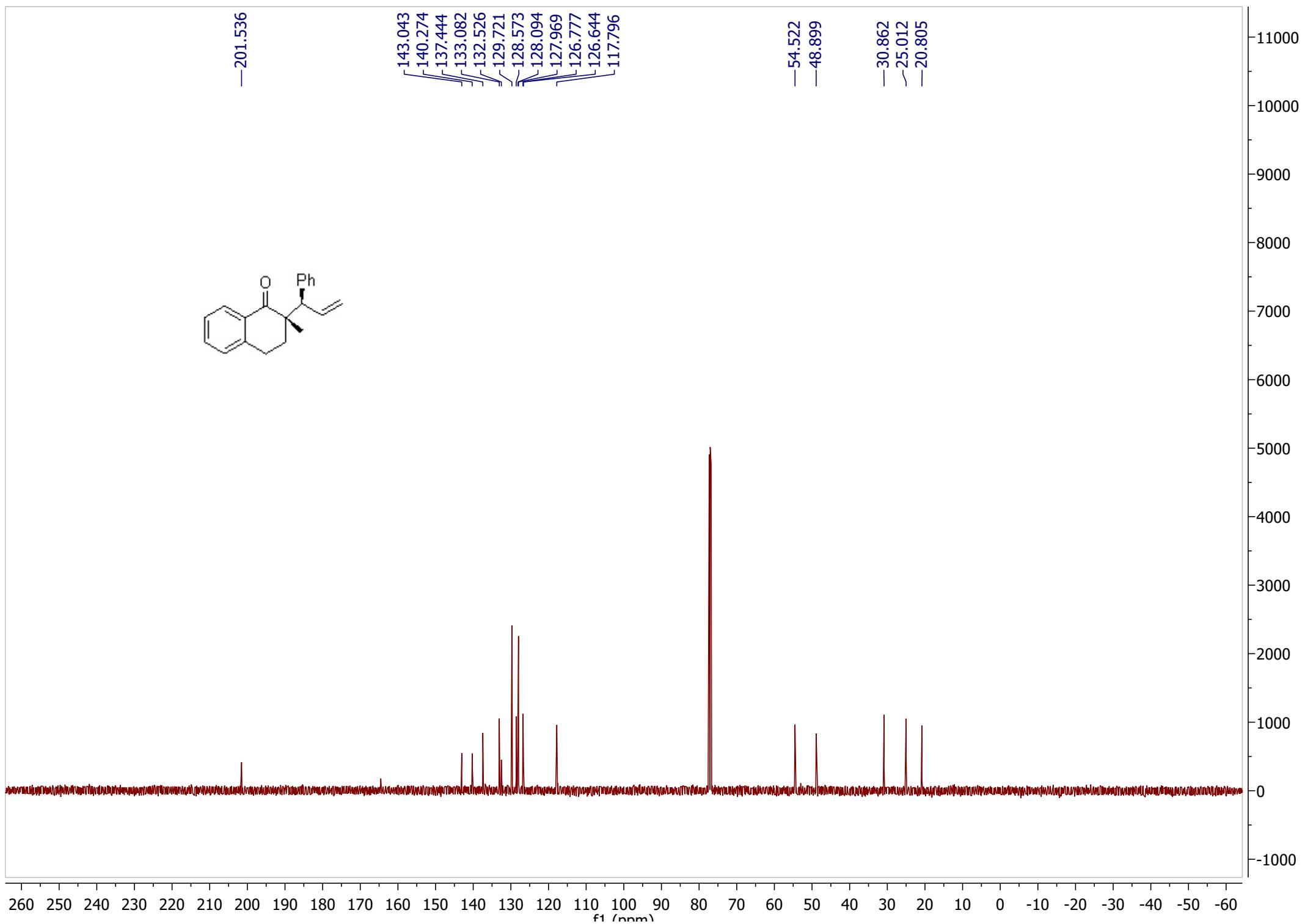
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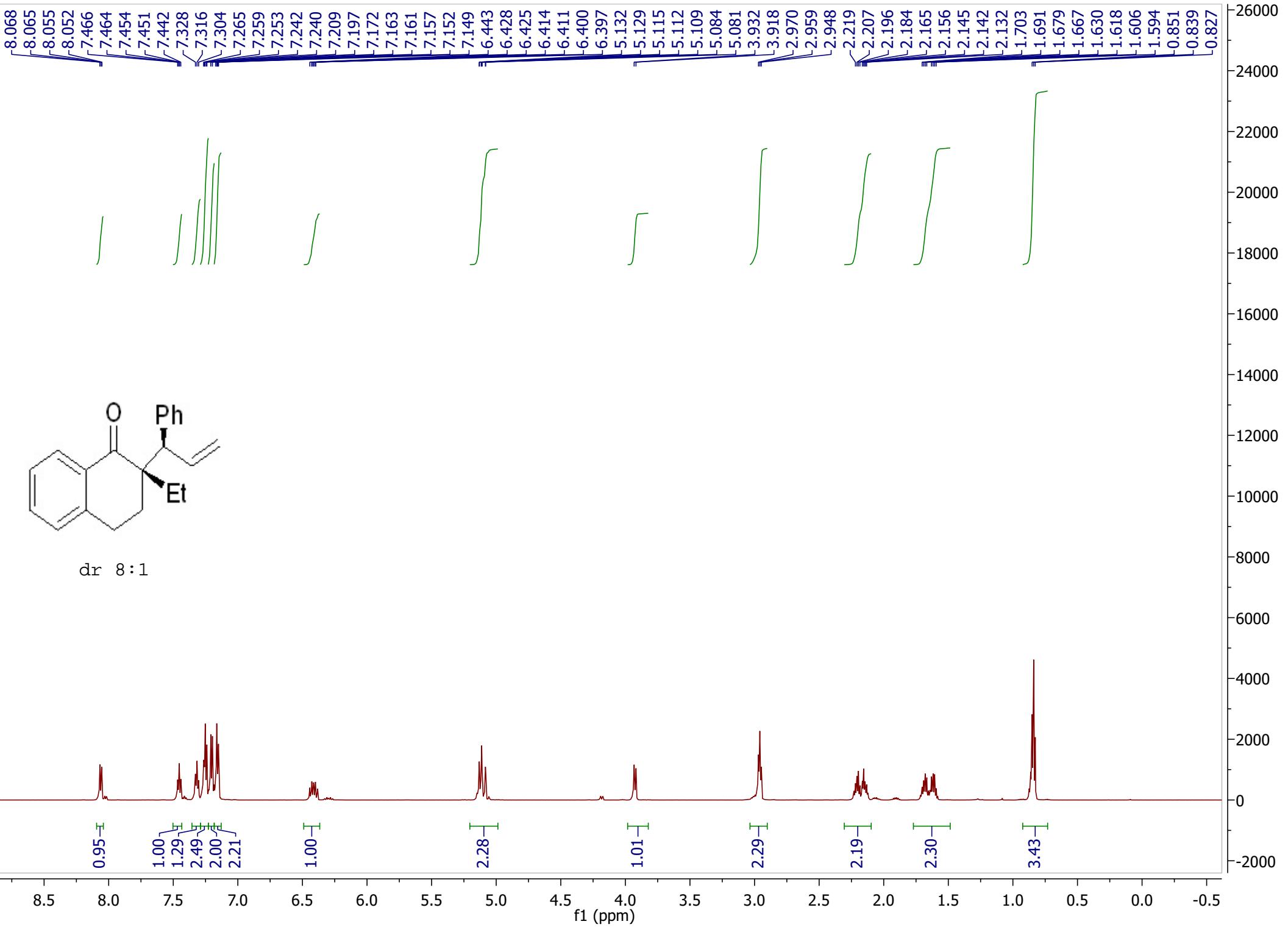


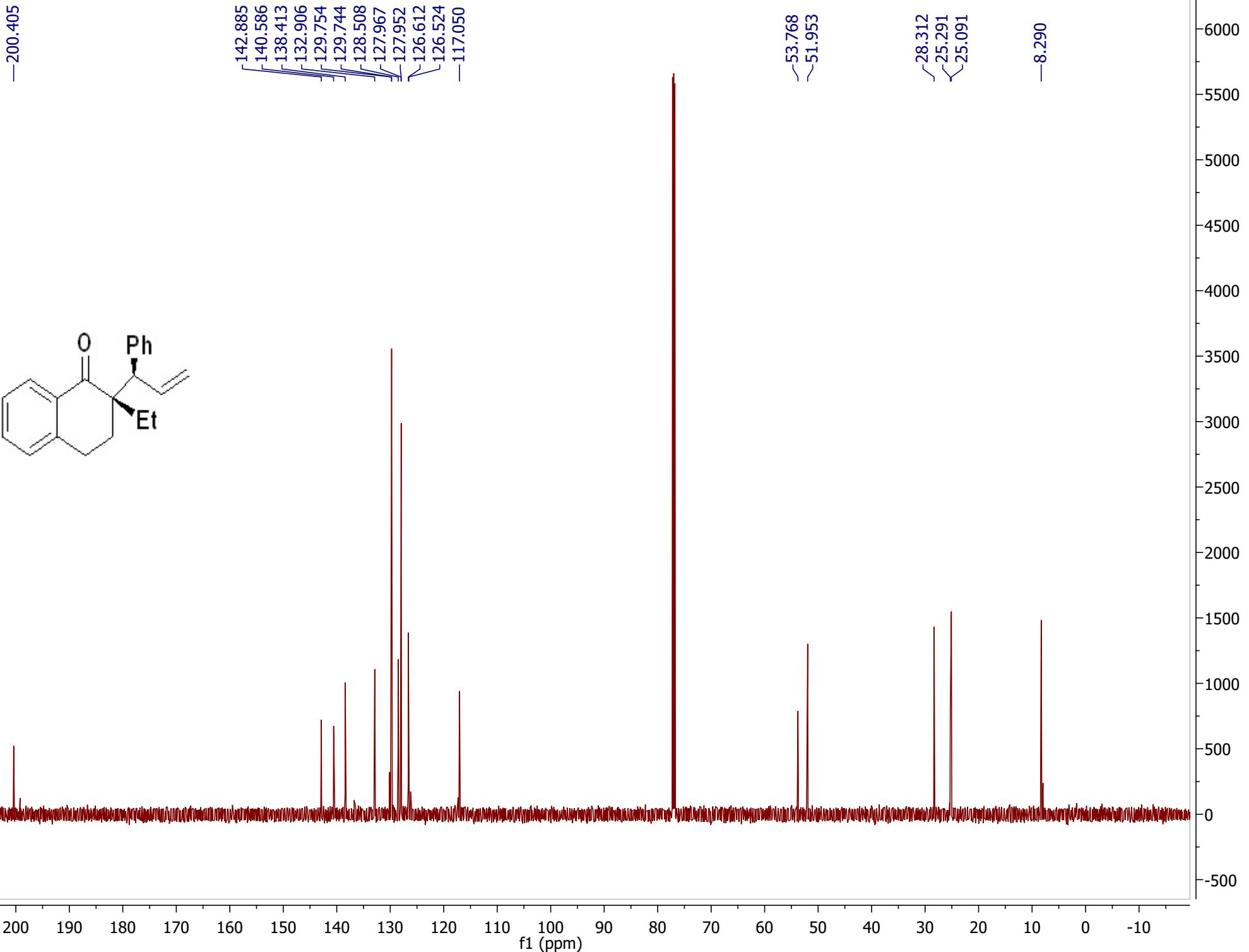
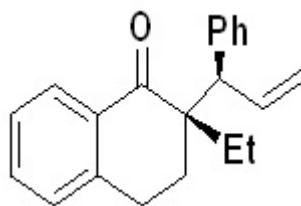
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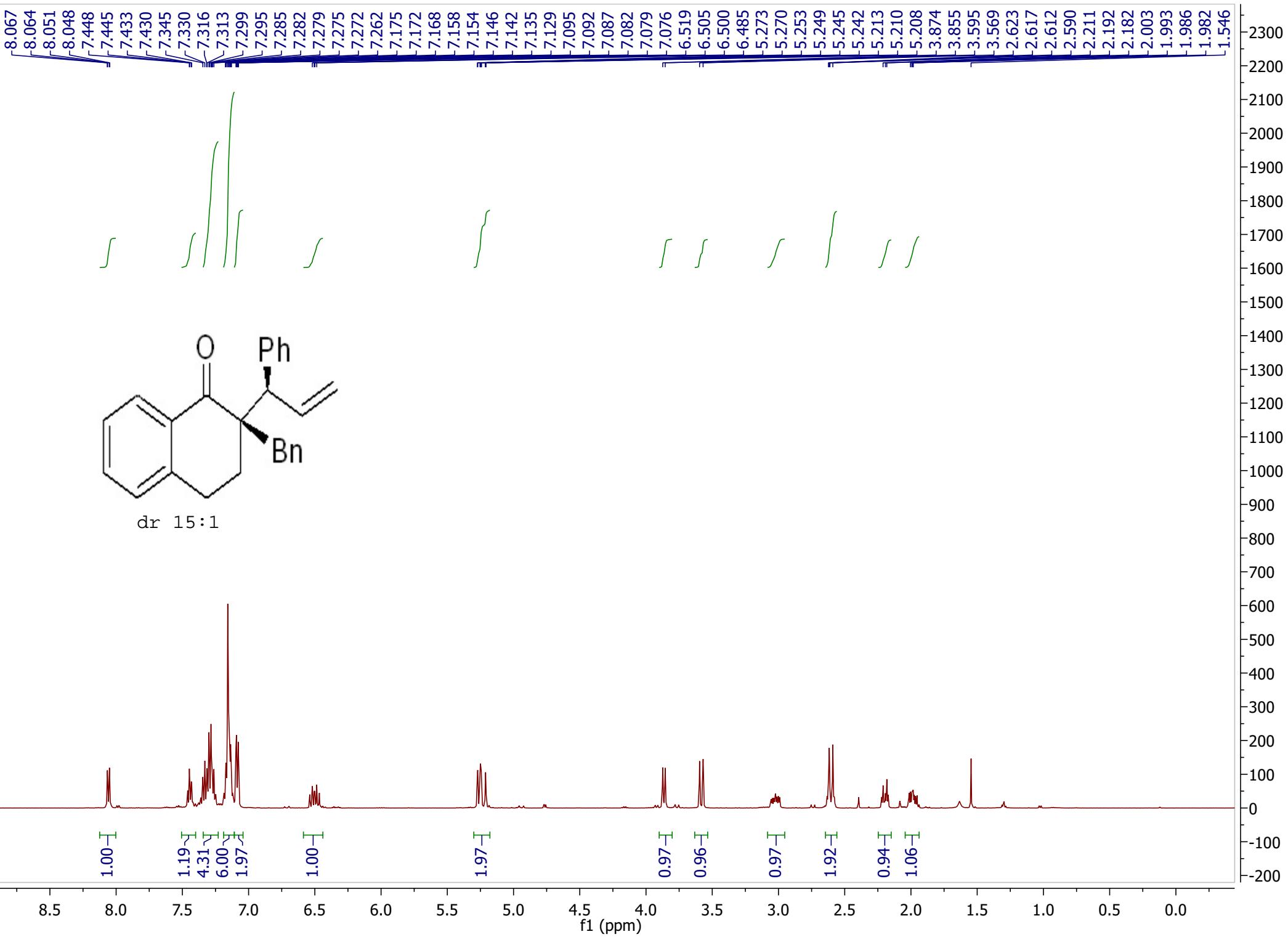
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126.644
117.796

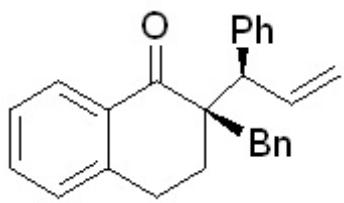
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—48.899
—30.862
—25.012
—20.805







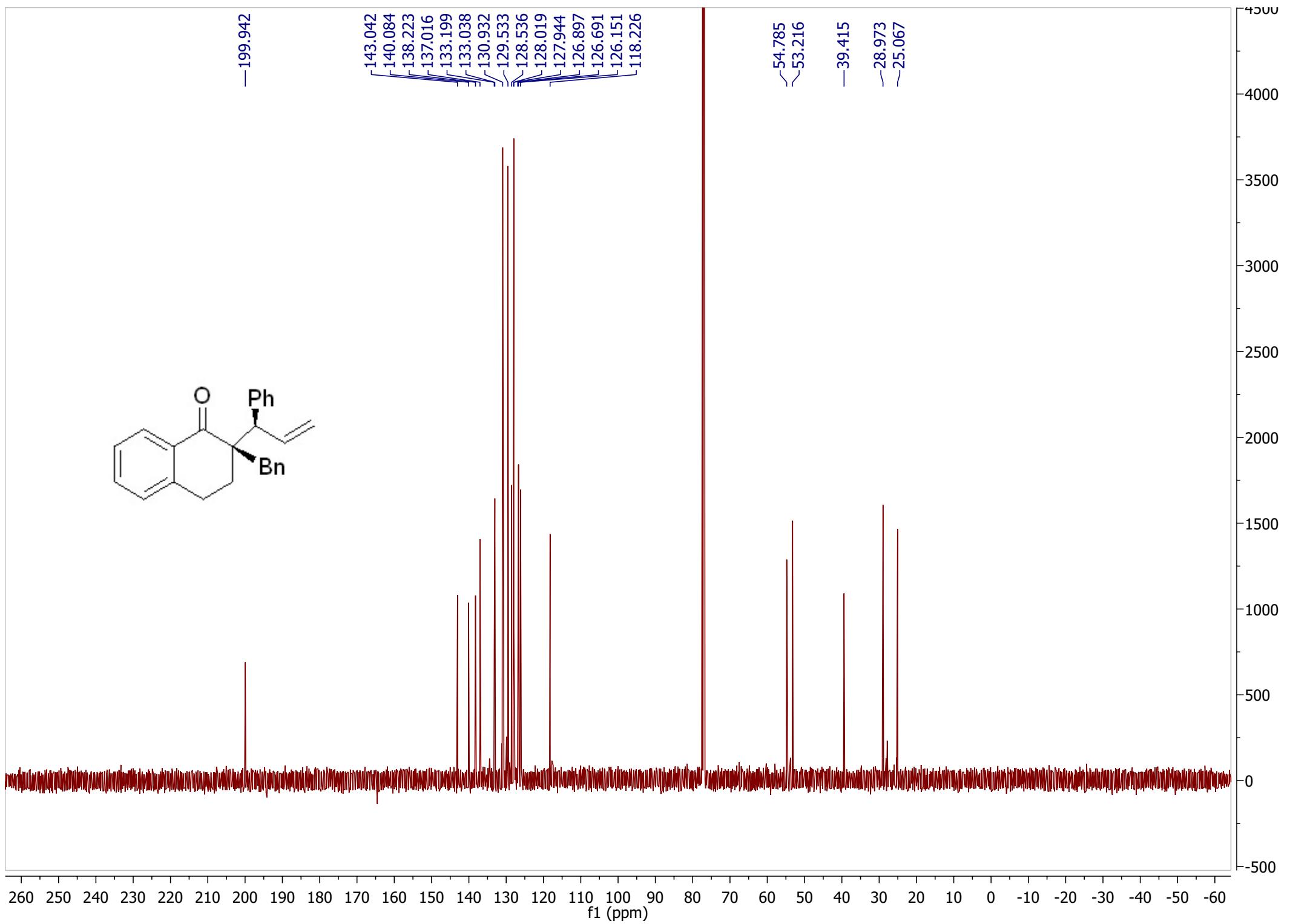


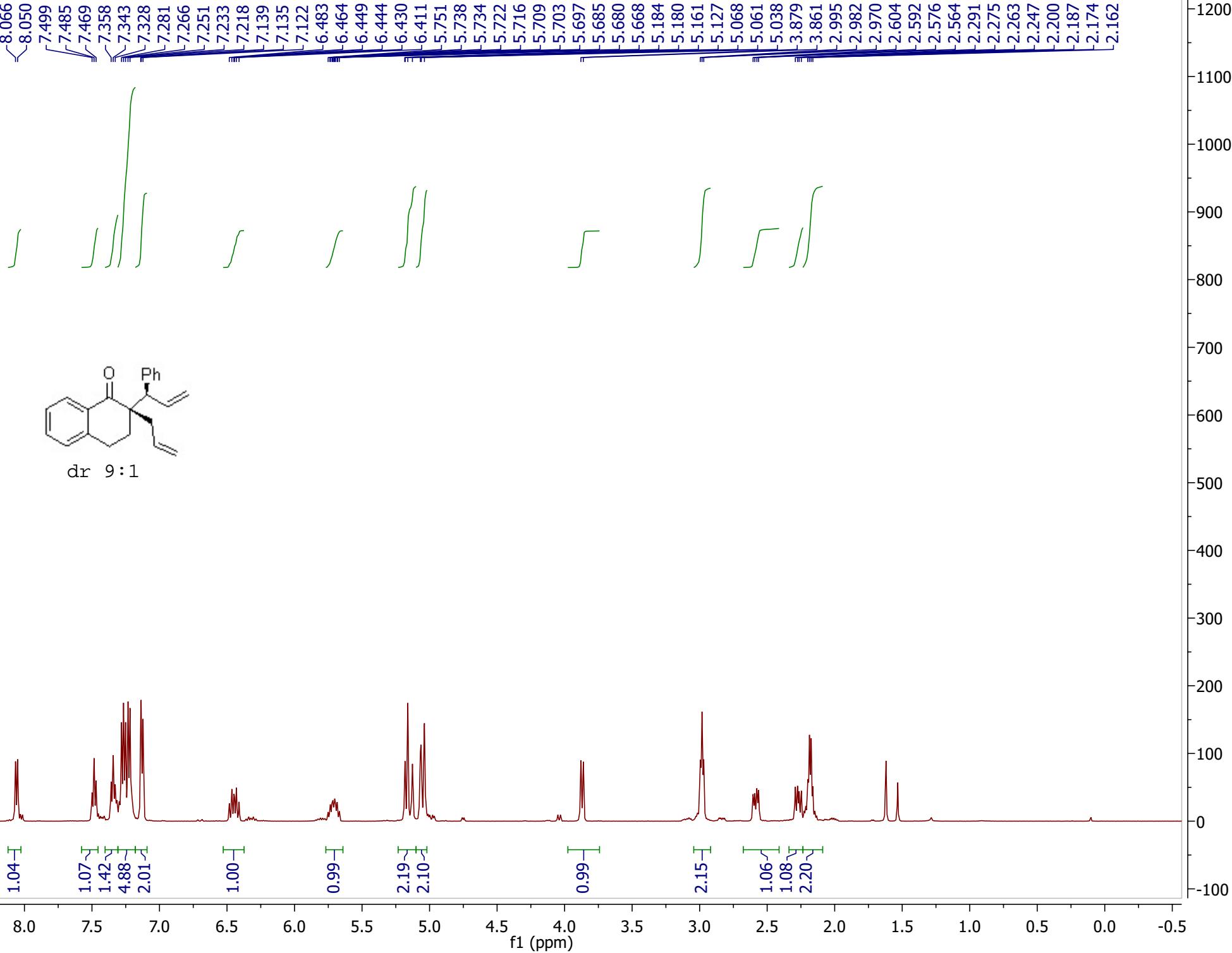


—199.942

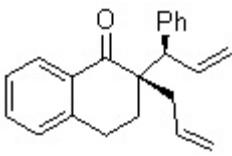
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126.691
126.151
118.226

54.785
53.216
—39.415
—28.973
—25.067





-200.135



142.981
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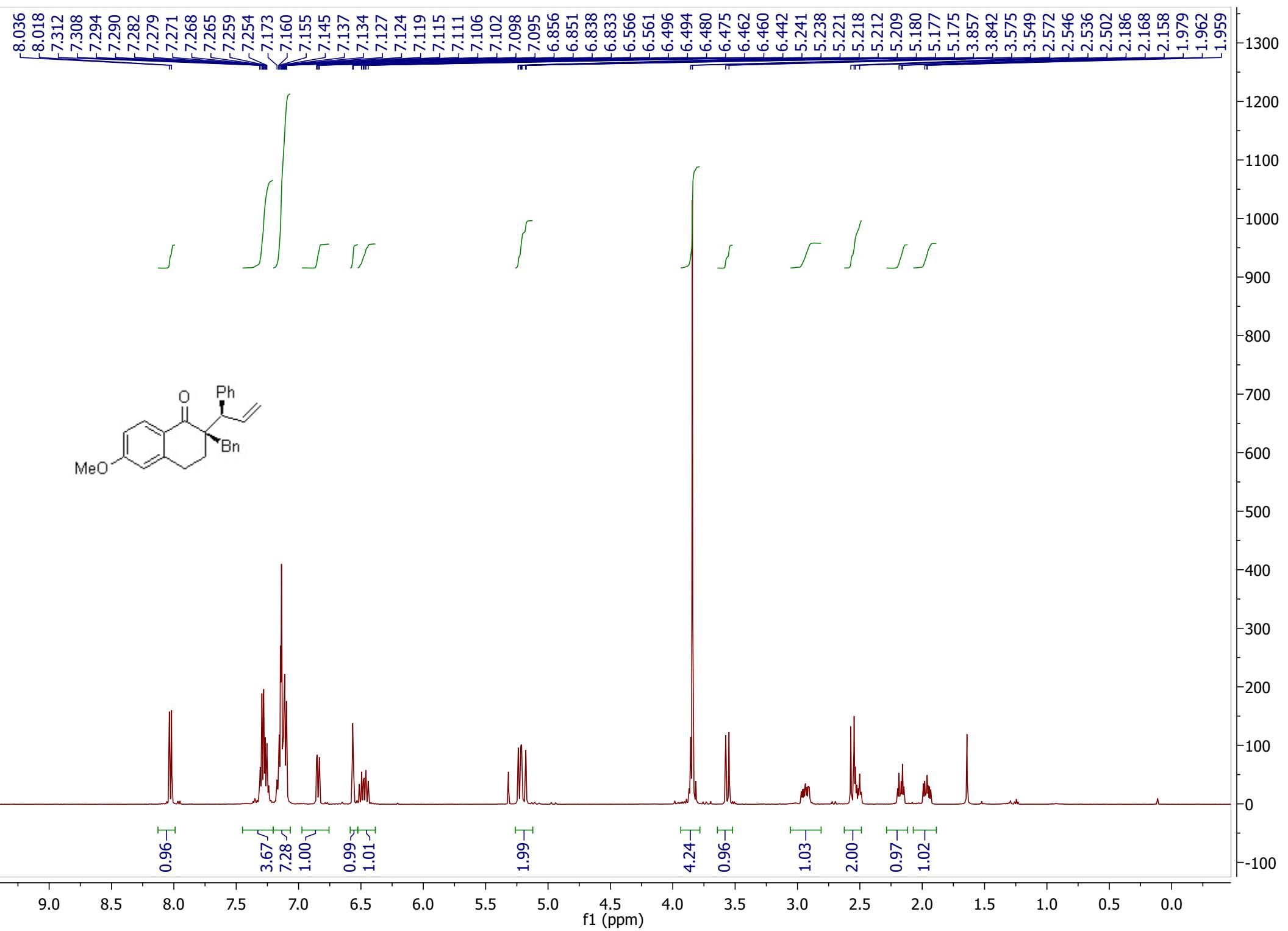
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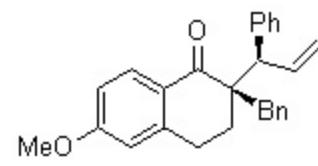
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f1 (ppm)

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4
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-6
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-12
-14
-16

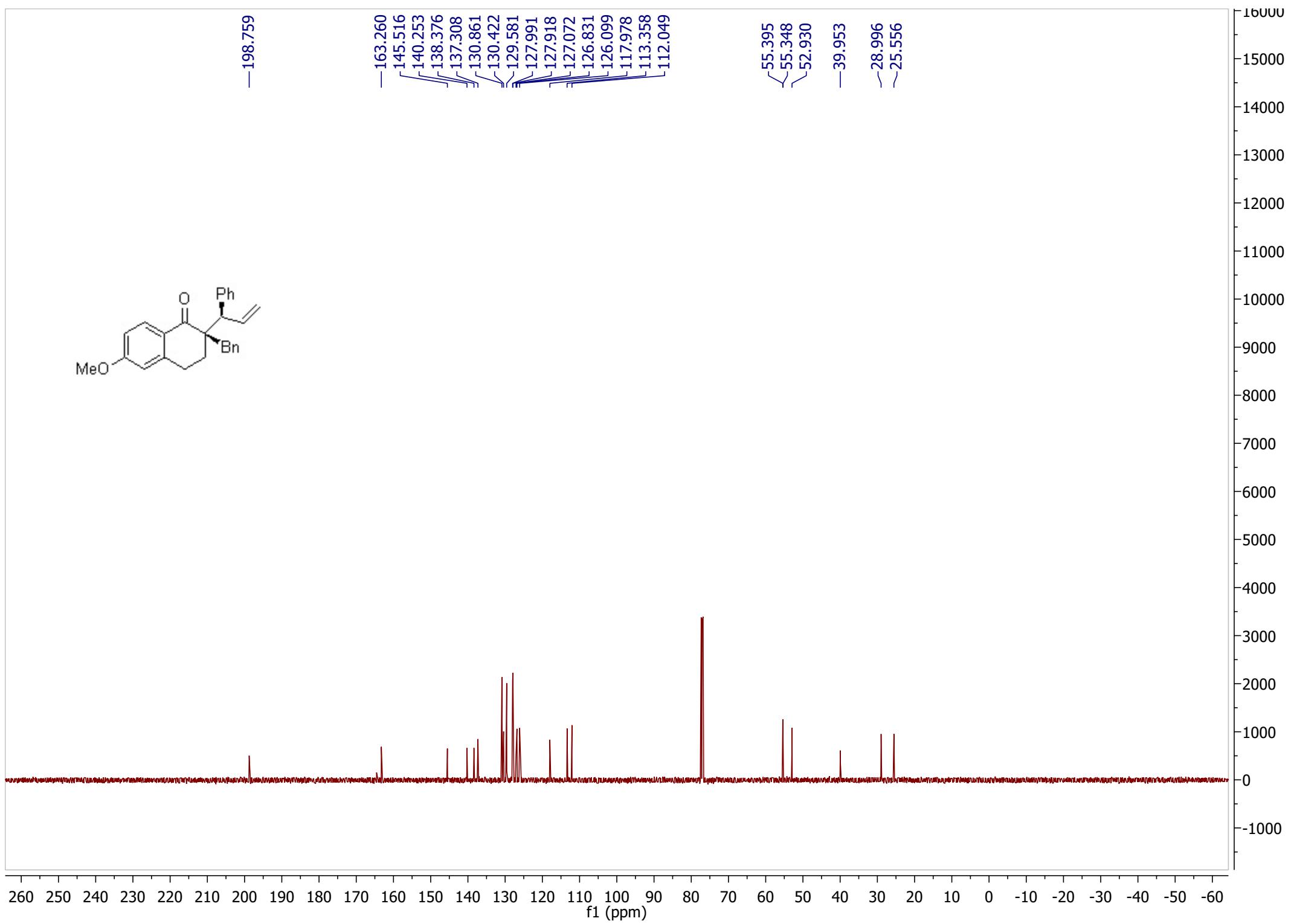


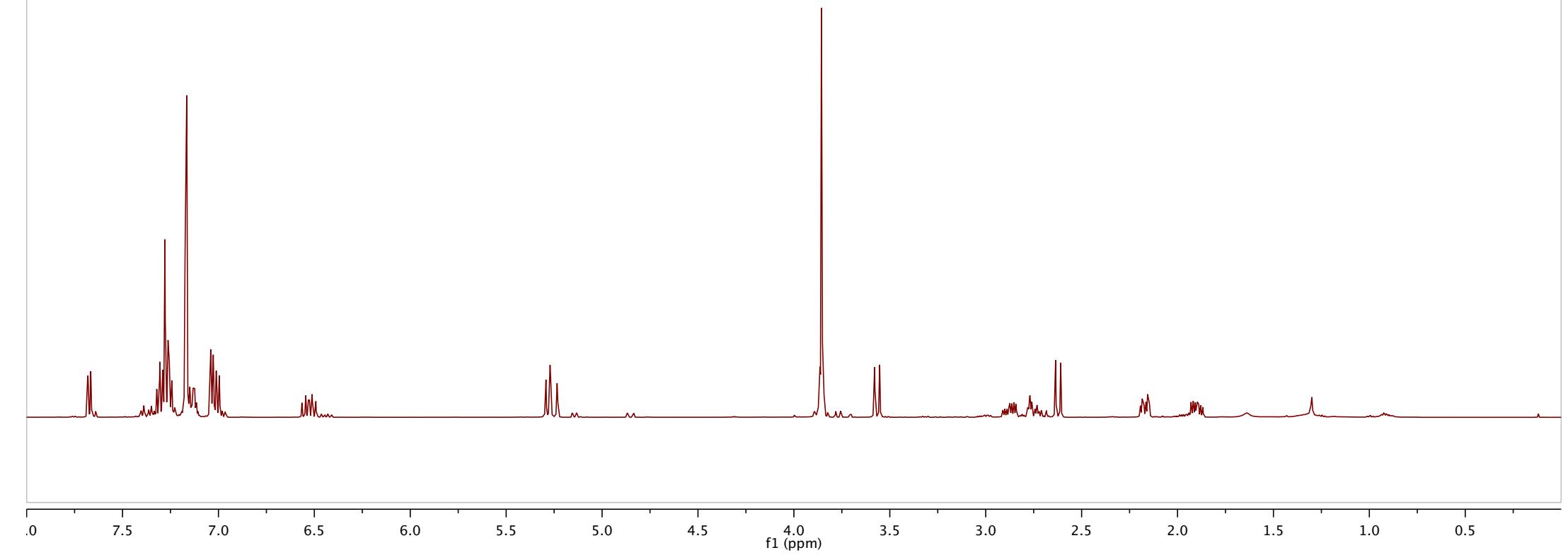
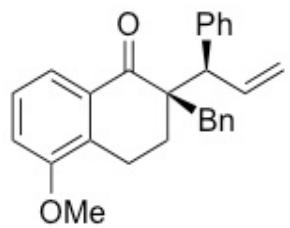


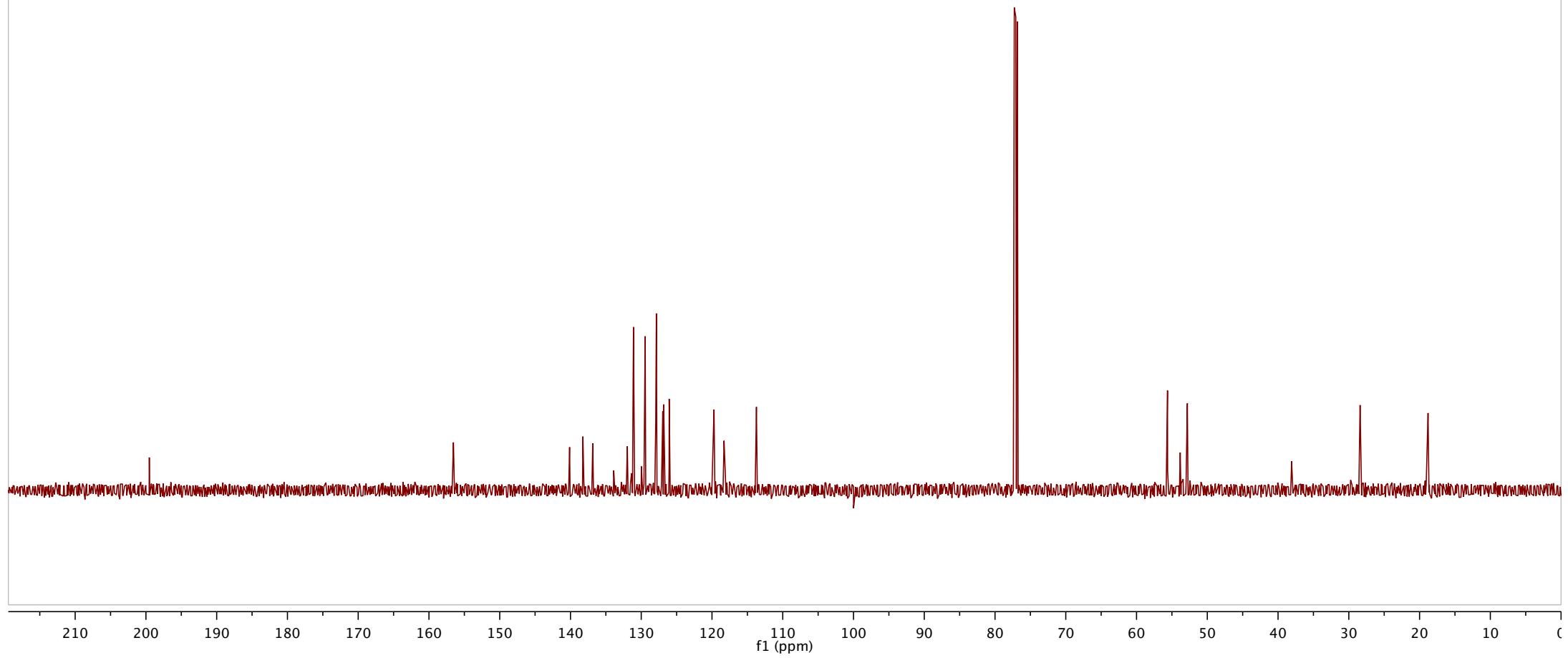
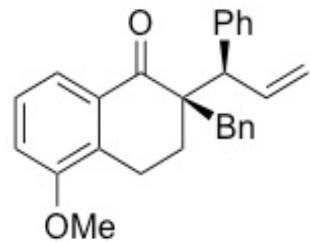
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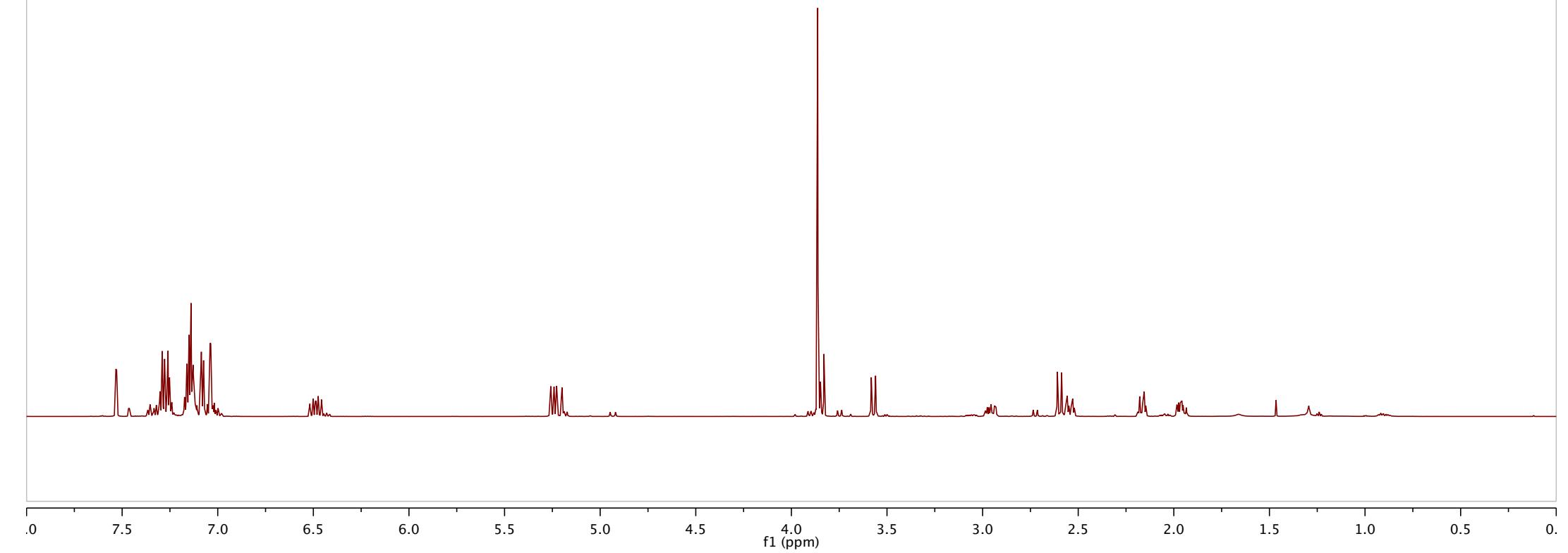
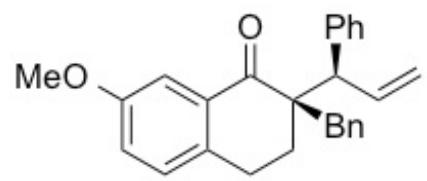
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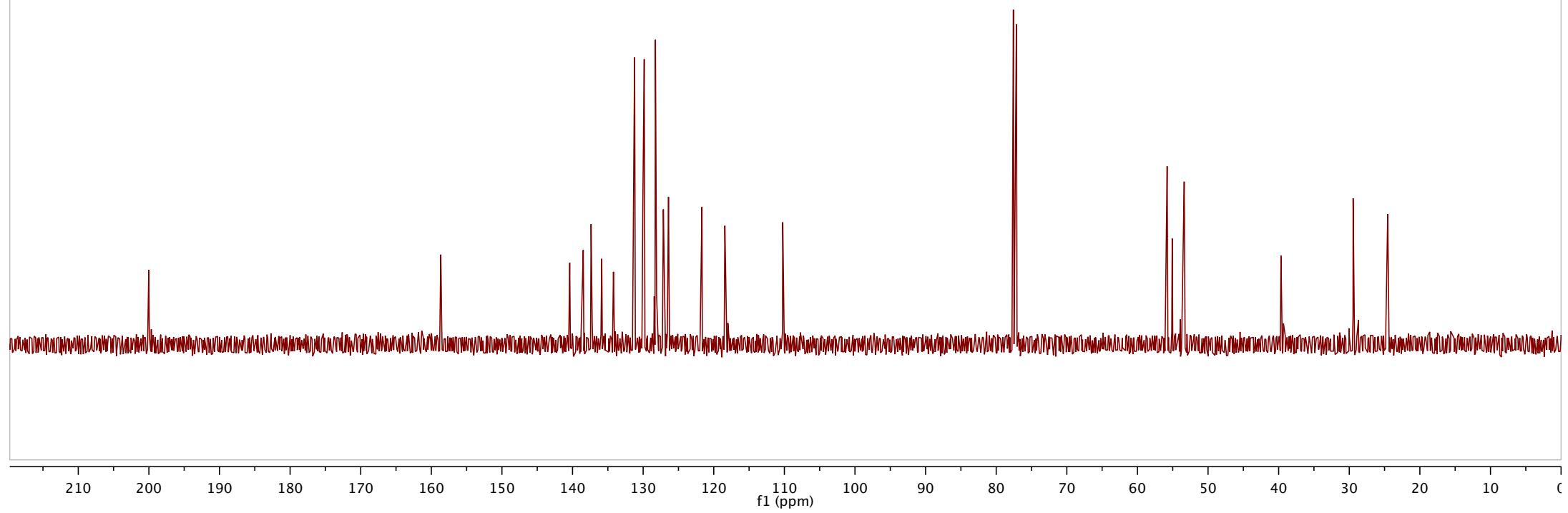
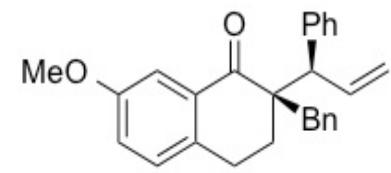
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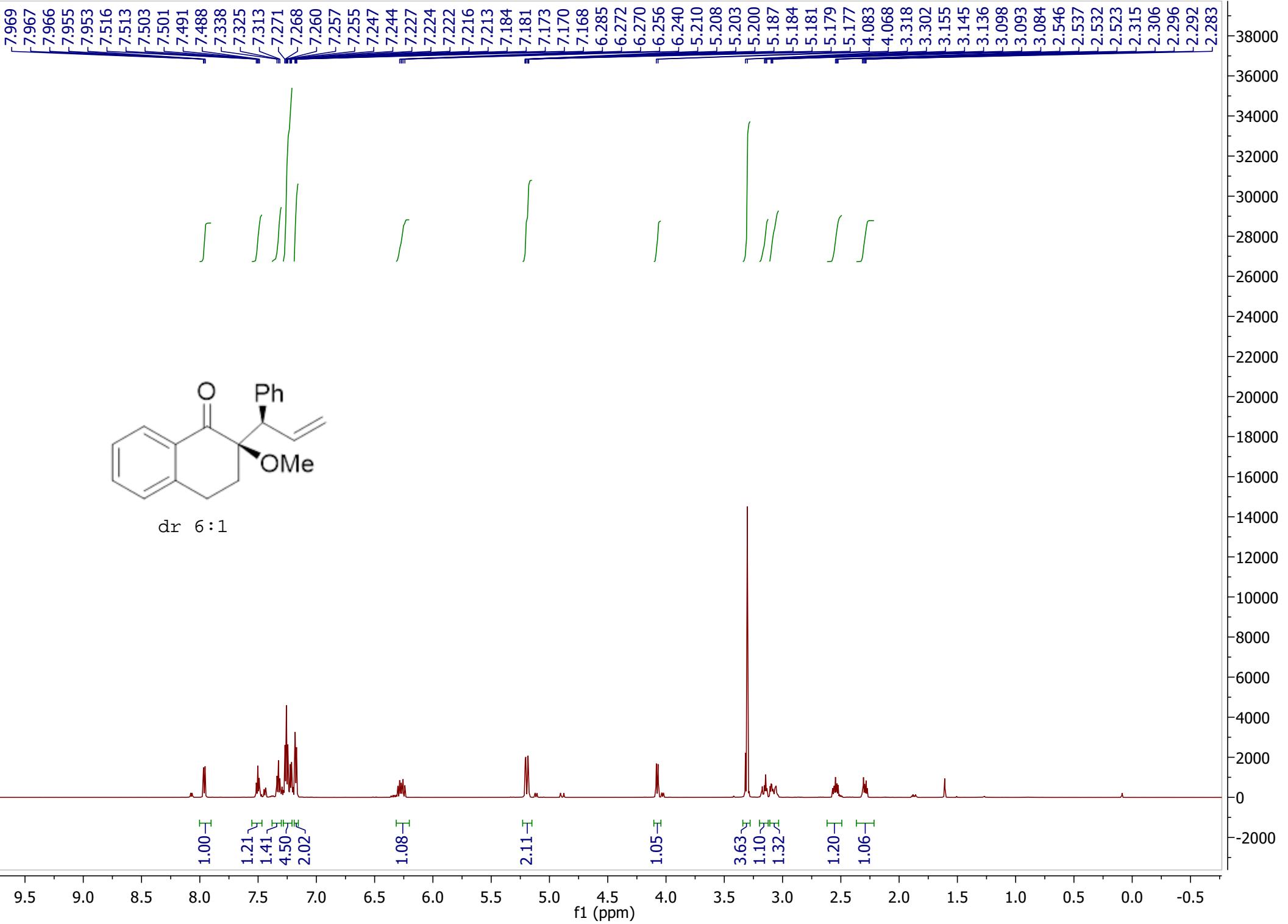




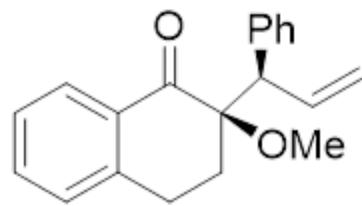








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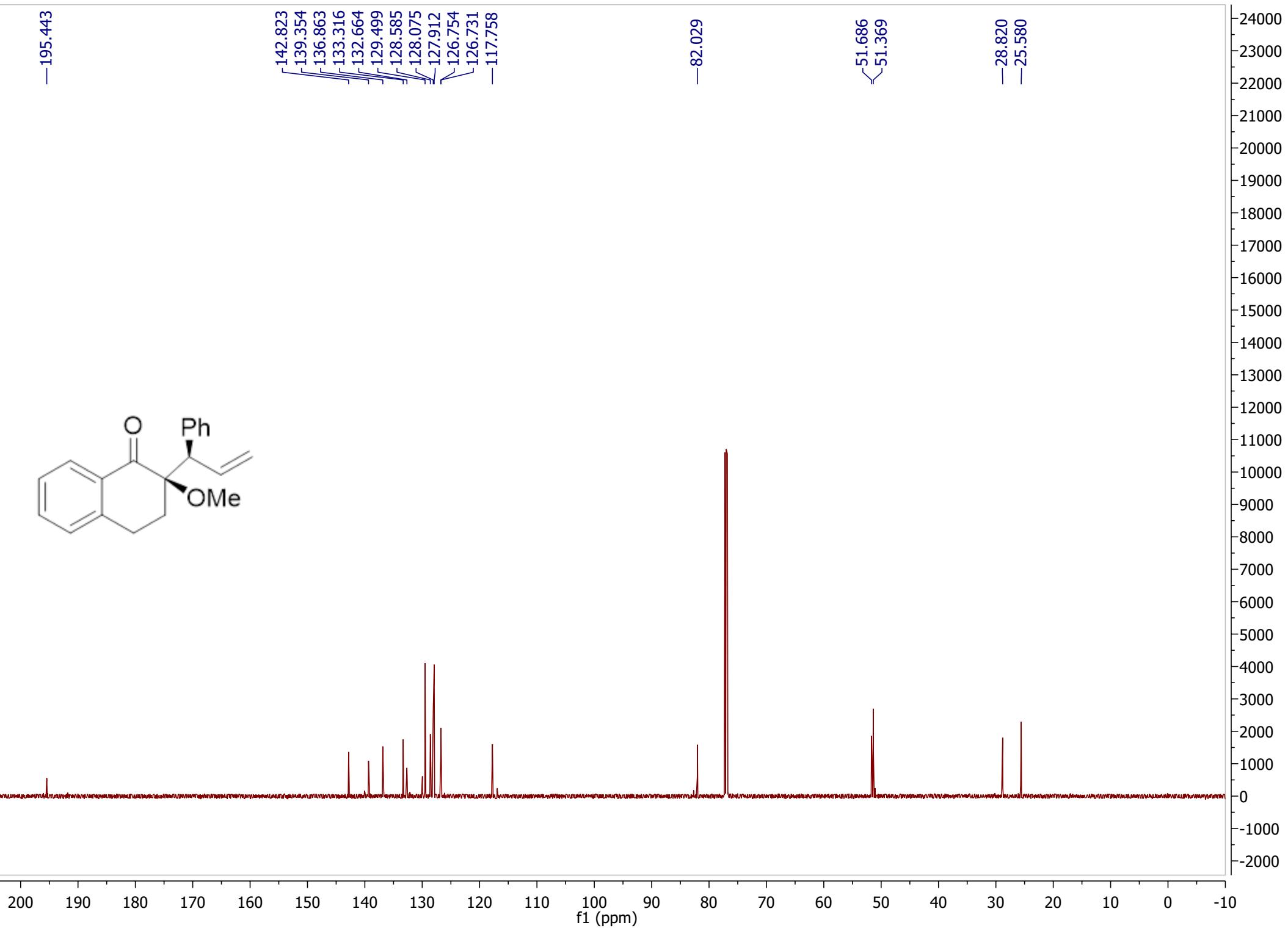


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-82.029

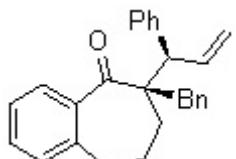
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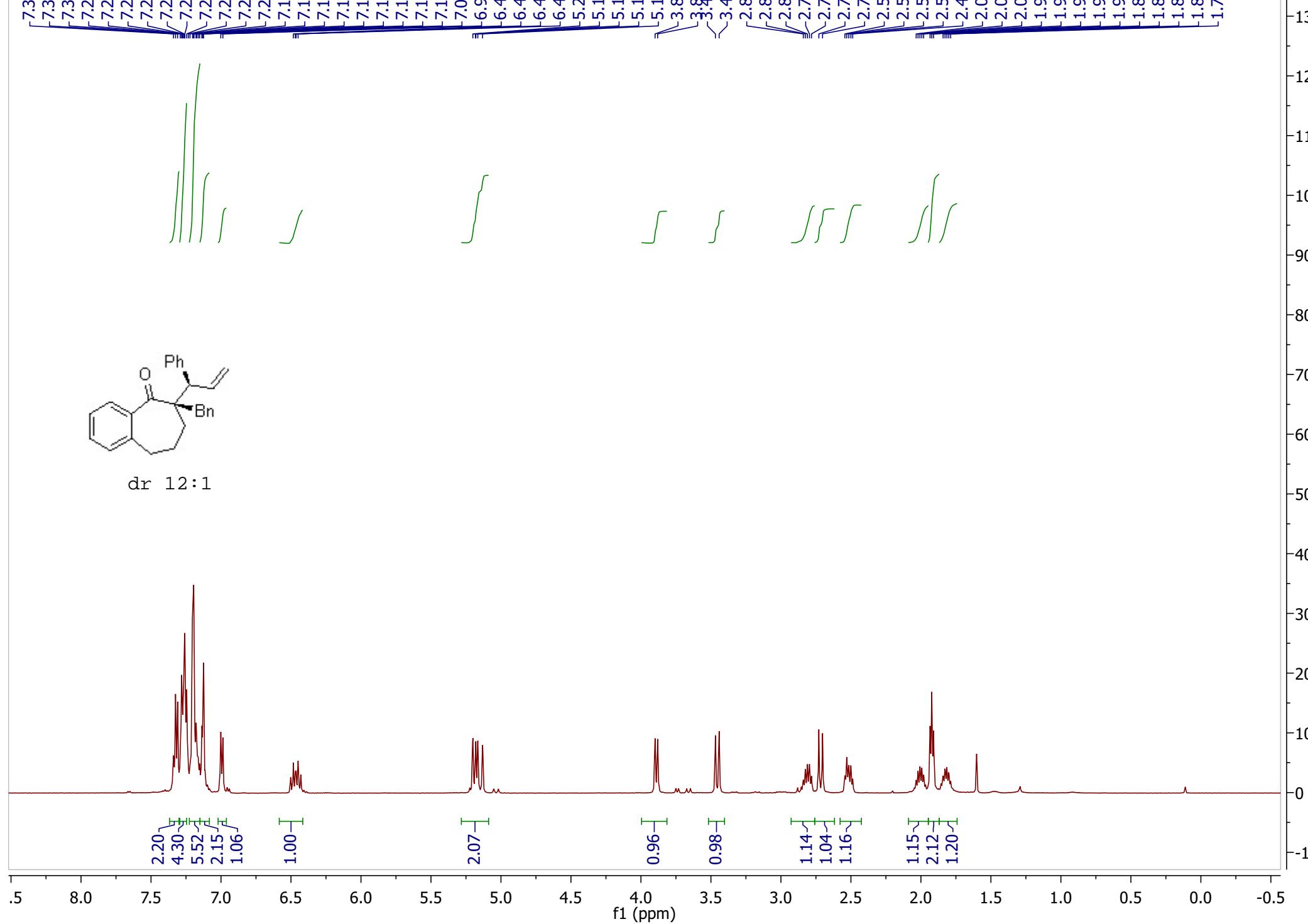


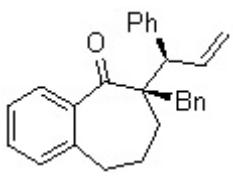
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 7.192
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 7.137
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 2.530
 2.515
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 2.034
 2.021
 2.007
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 1.935
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 1.910
 1.842
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 1.815
 1.801
 1.787

1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100



dr 12:1





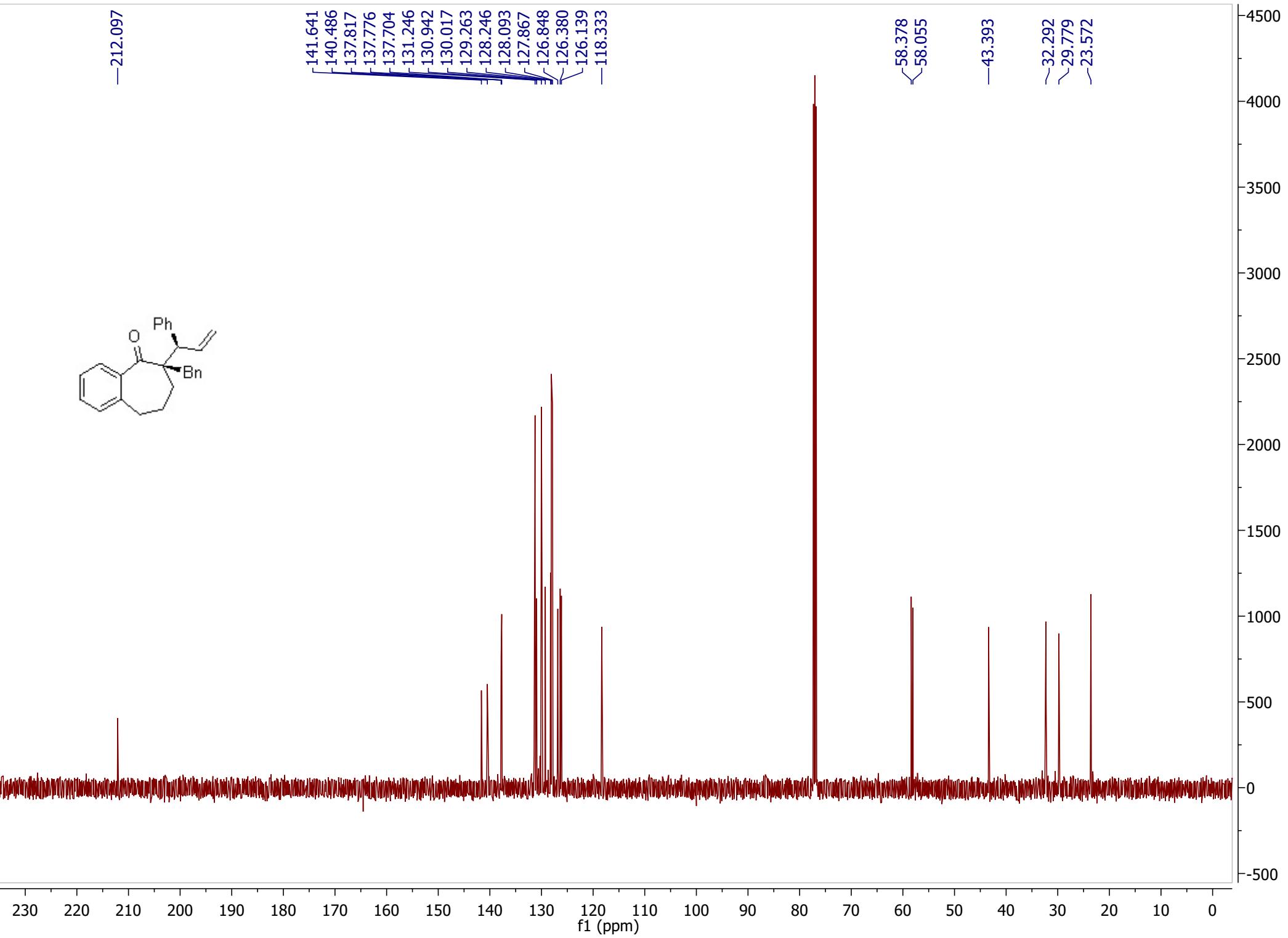
-212.097

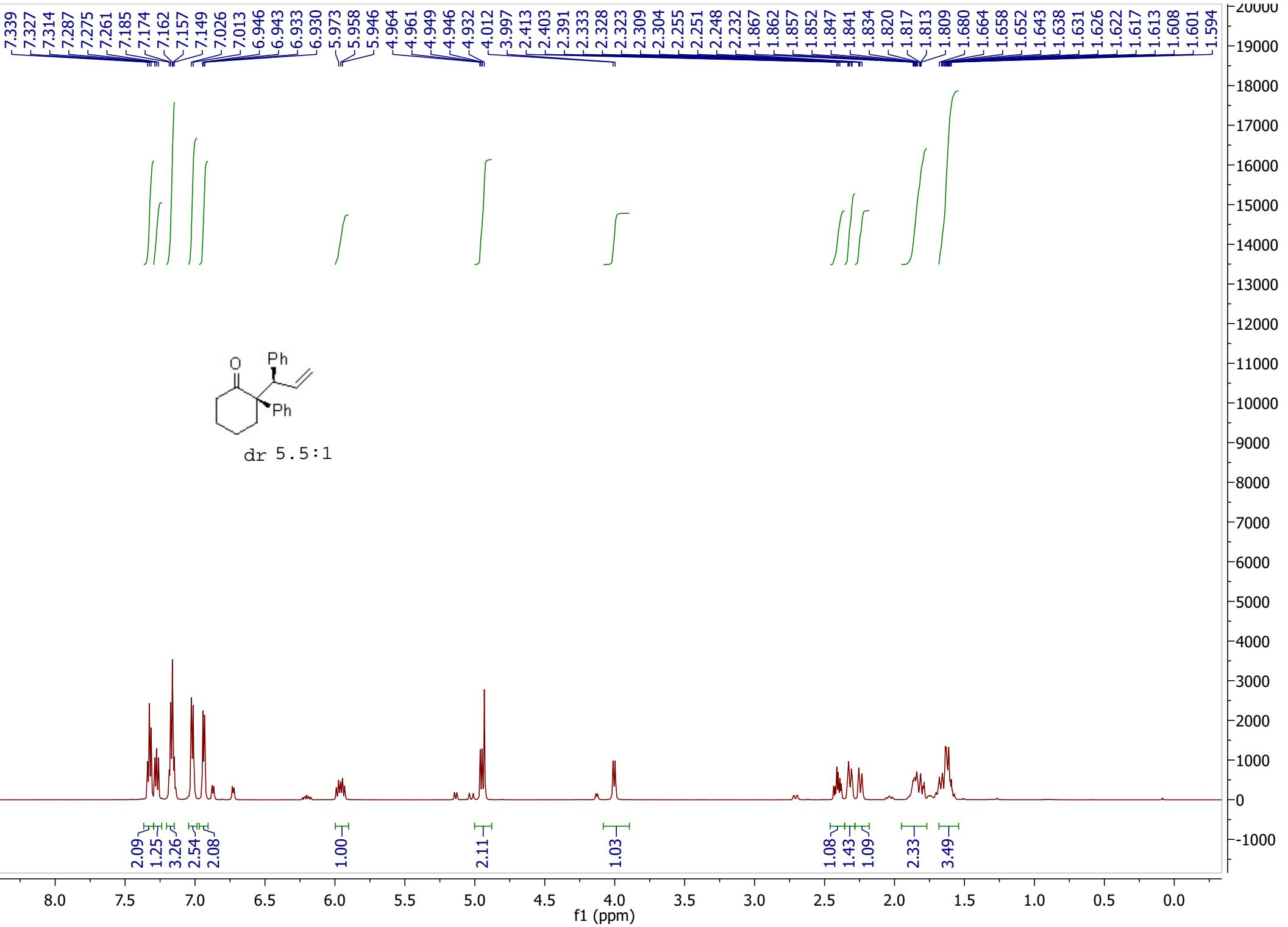
141.641
140.486
137.817
137.776
137.704
131.246
130.942
130.017
129.263
128.246
128.093
127.867
126.848
126.380
126.139
-118.333

58.378
58.055

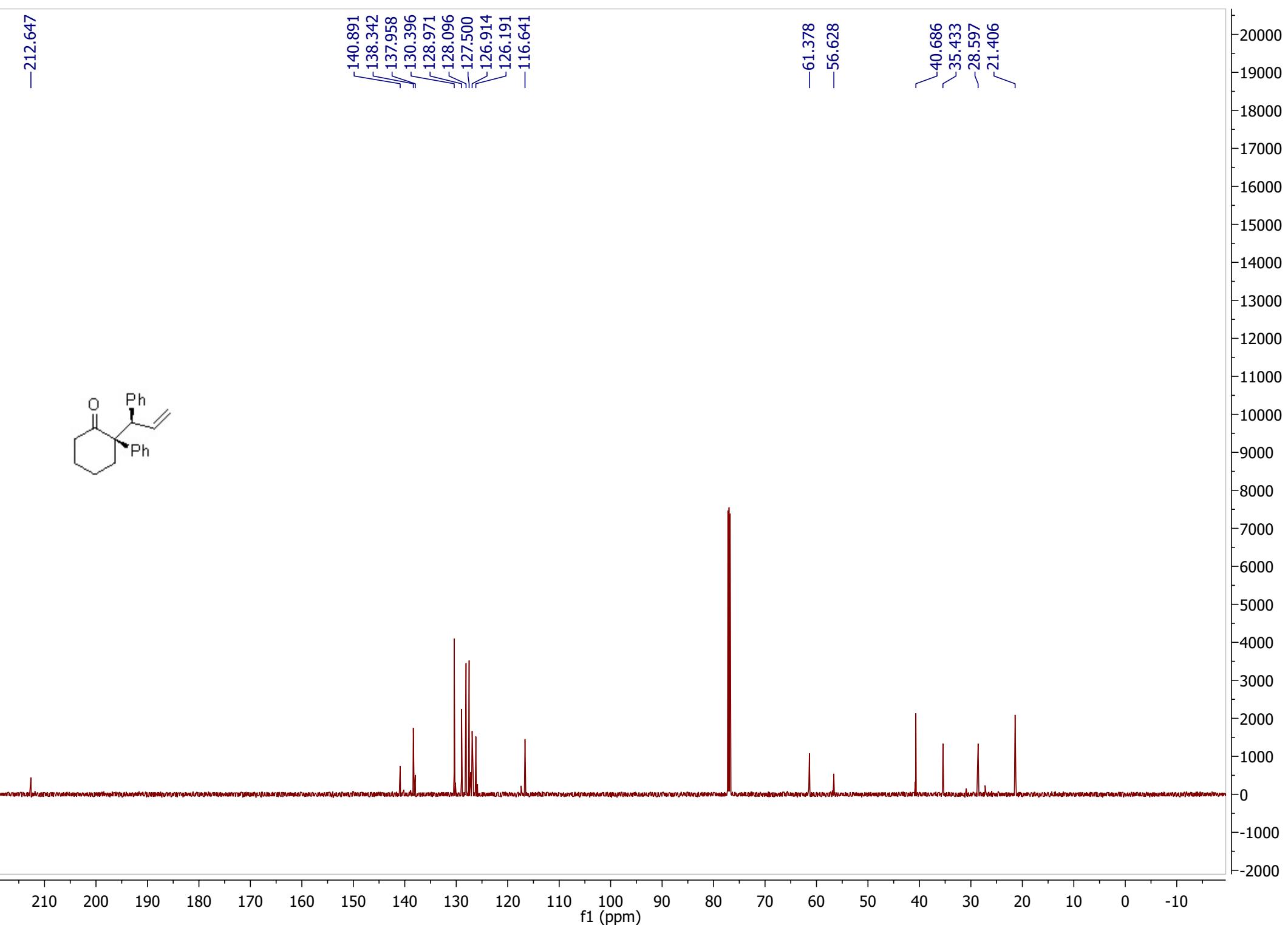
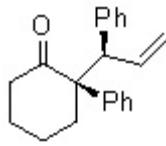
-43.393

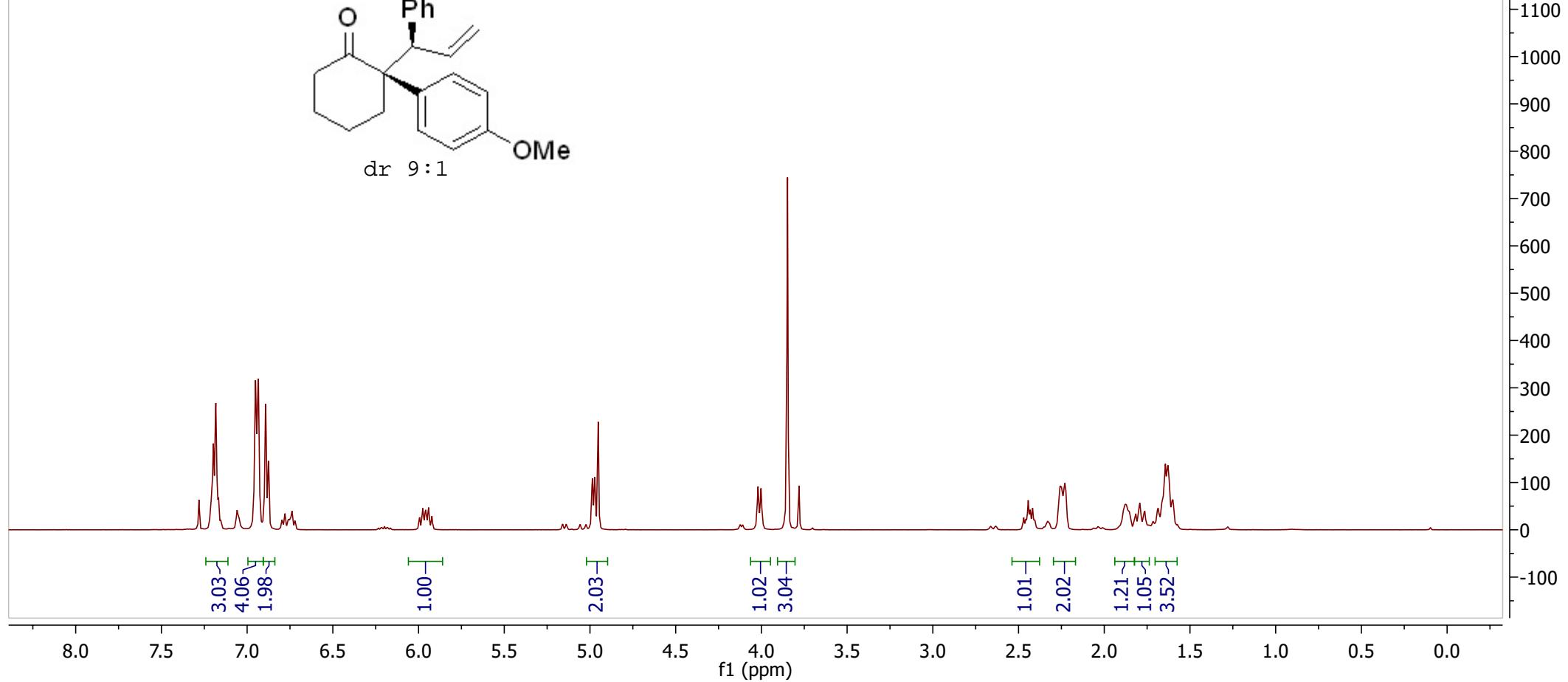
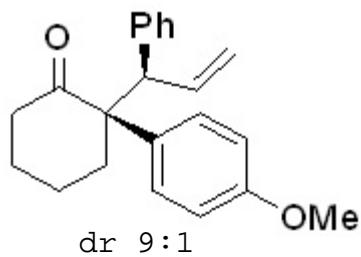
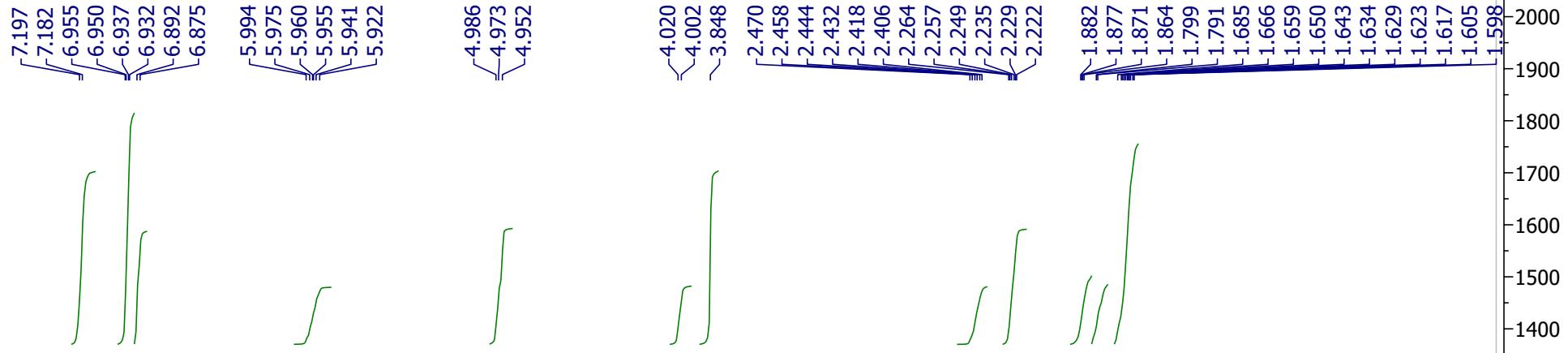
~32.292
~29.779
~23.572



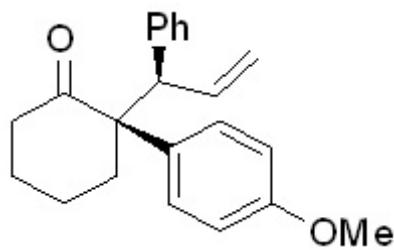


-212.647





—212.987



—158.416

—140.974
—138.505
—130.389
—130.091
—127.504
—126.166
—116.578
—113.429

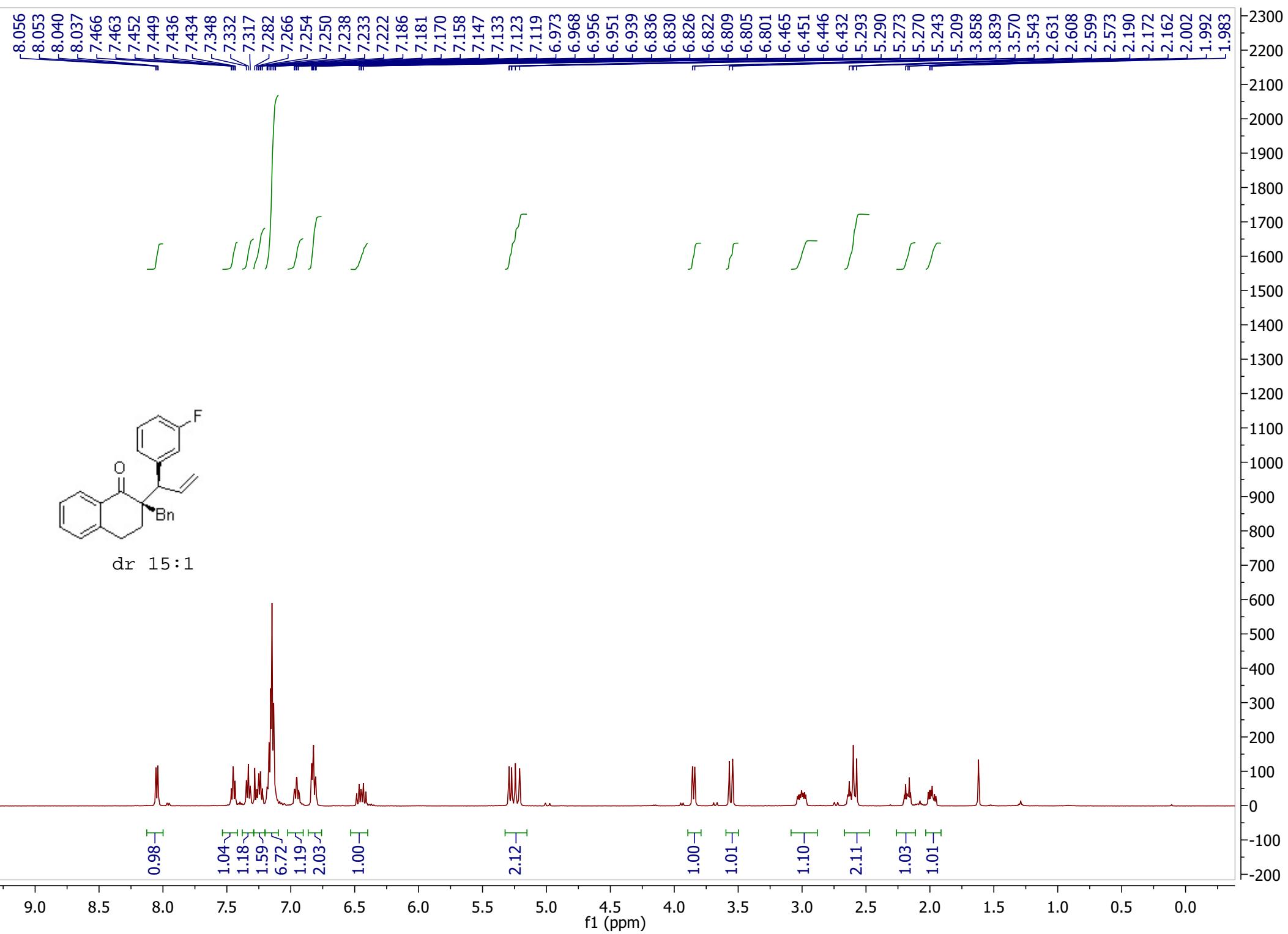
—60.563
—56.439
—55.180

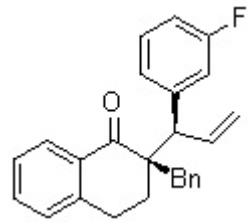
—40.479
—35.705
—28.664
—21.346

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11





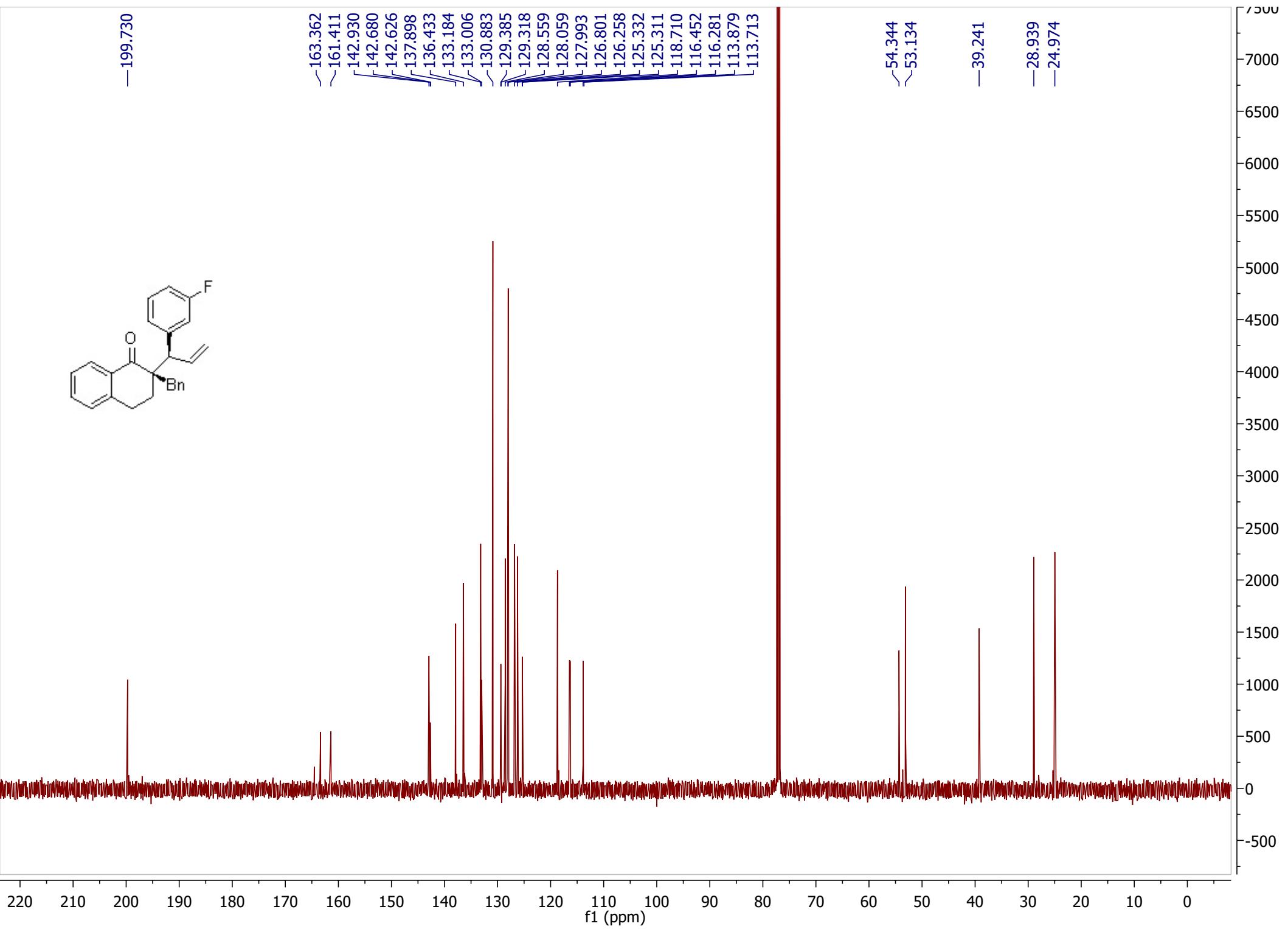
—199.730

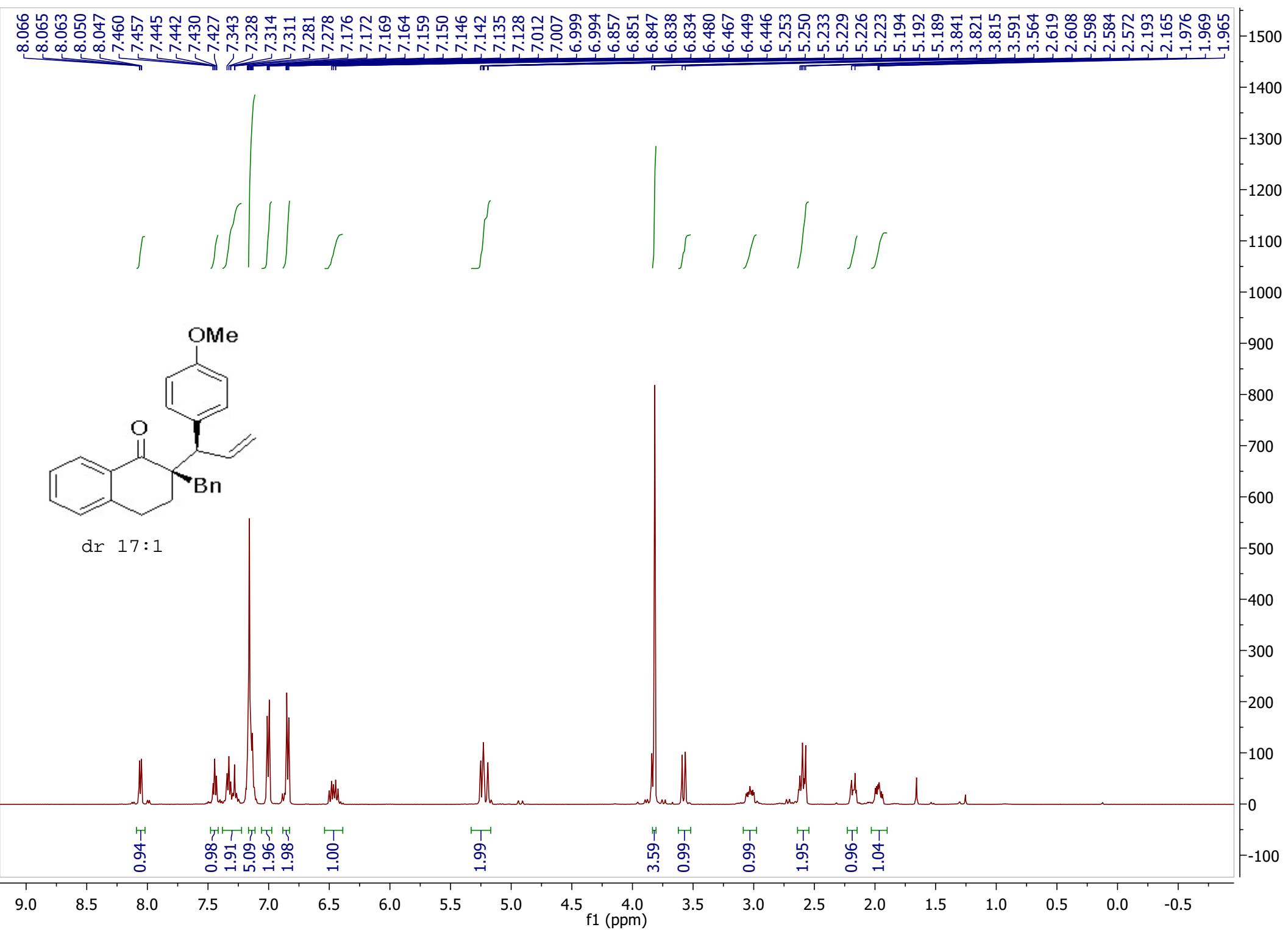
—163.362
—161.411
142.930
142.680
142.626
137.898
136.433
133.184
133.006
130.883
129.385
129.318
128.559
128.059
127.993
126.801
126.258
125.332
125.311
118.710
116.452
116.281
113.879
113.713

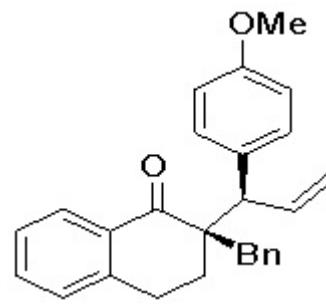
—54.344
—53.134

—39.241

—28.939
—24.974





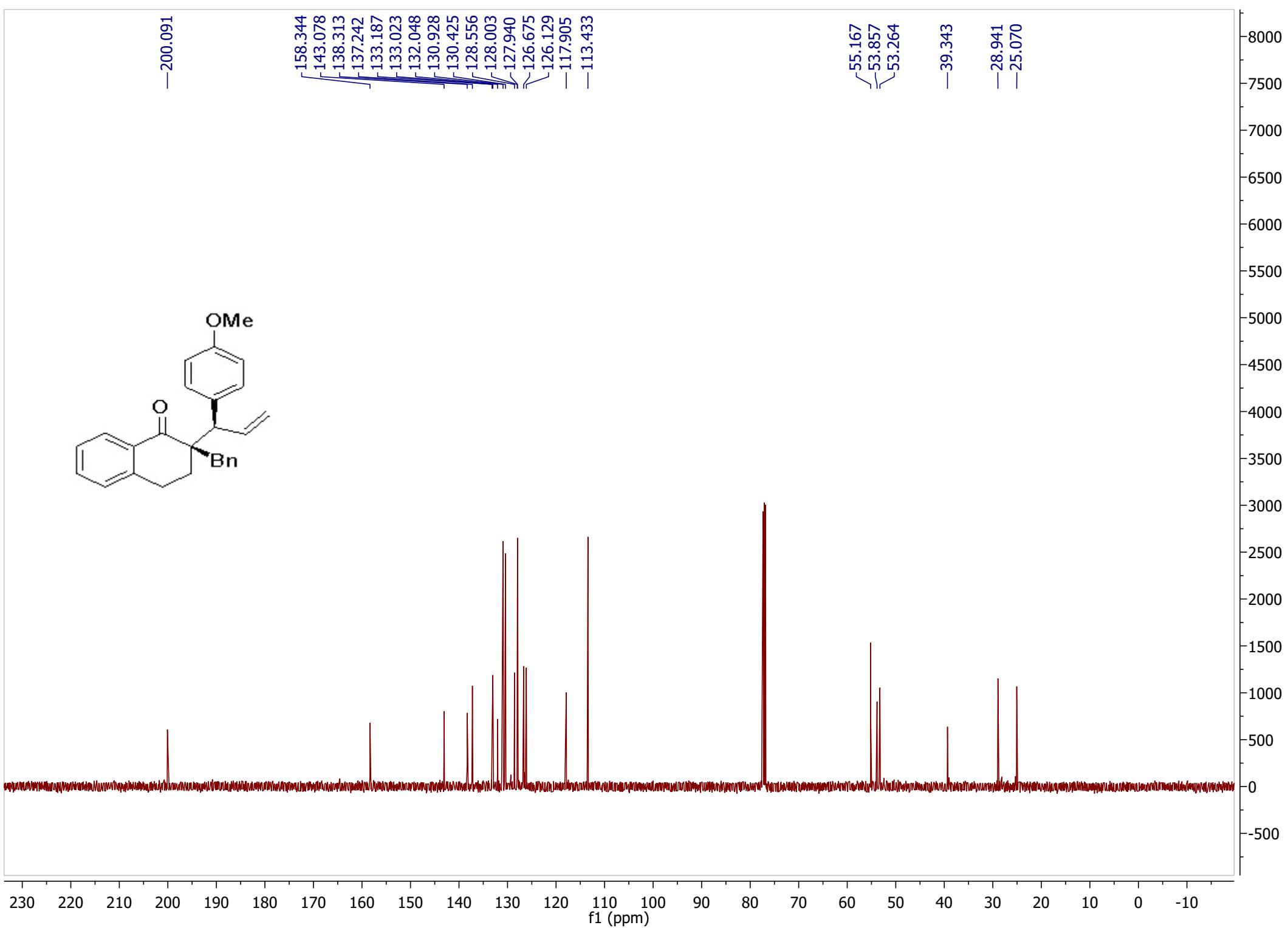


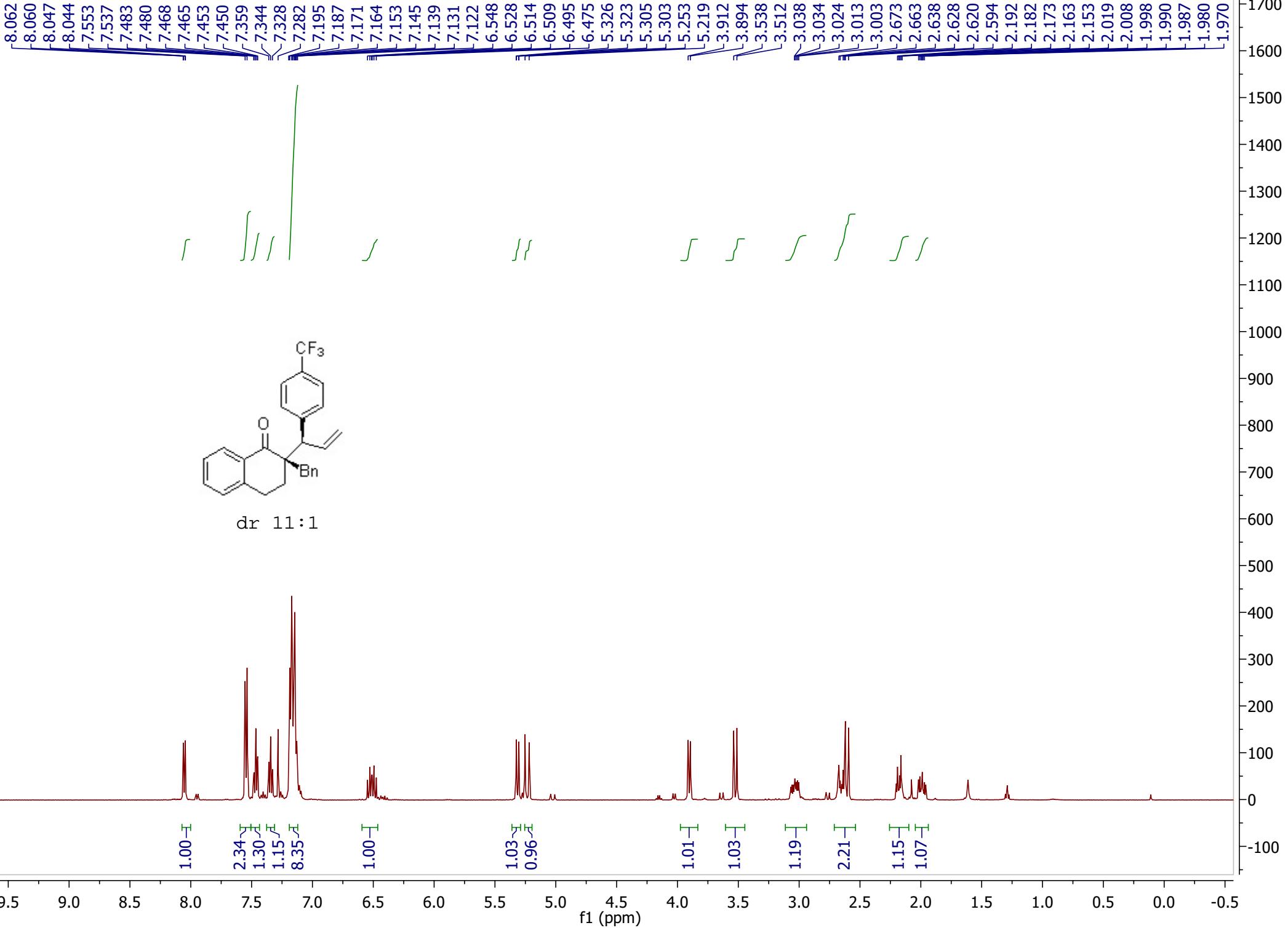
-200.091

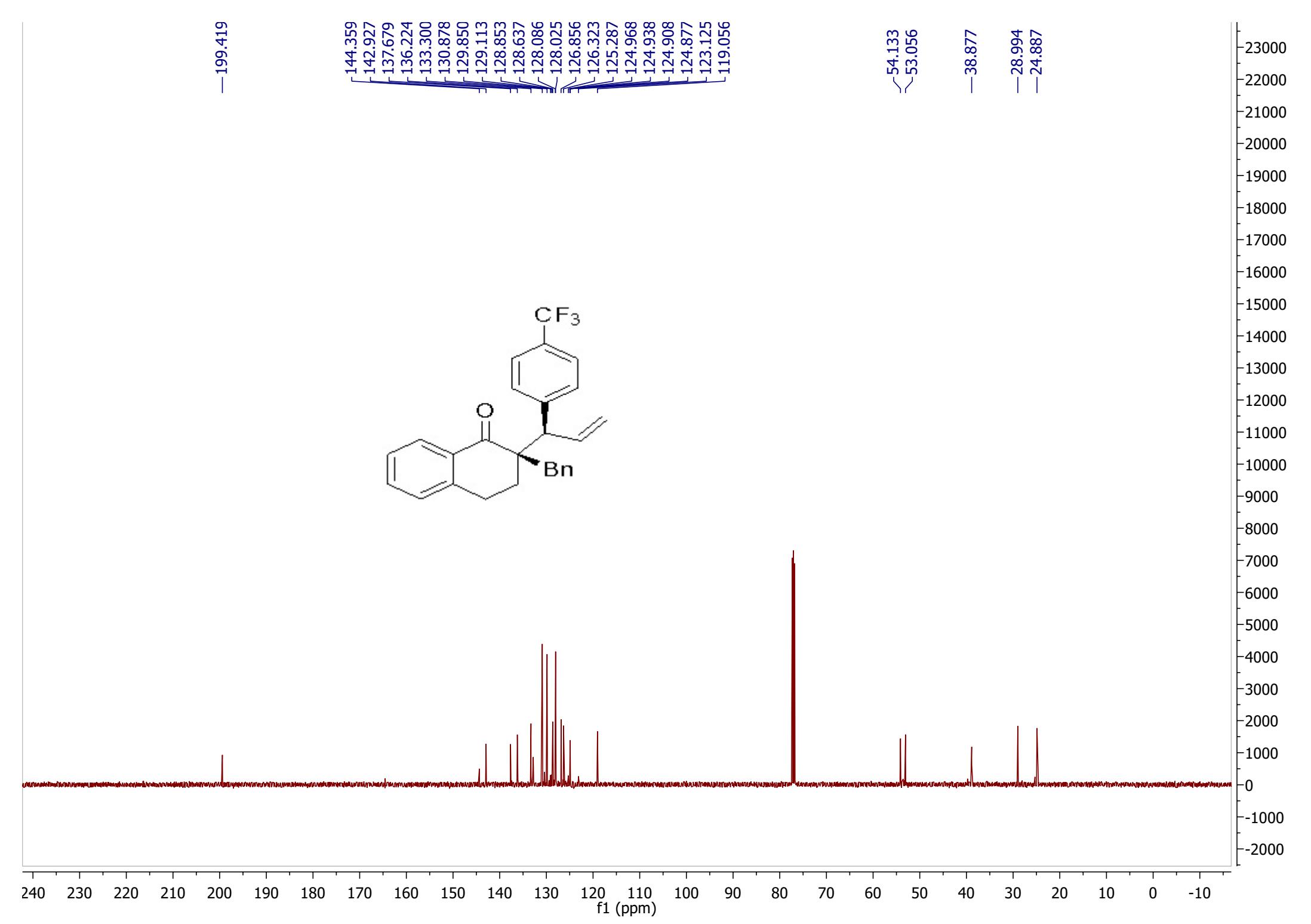
158.344
143.078
138.313
137.242
133.187
133.023
132.048
130.928
130.425
128.556
128.003
127.940
126.675
126.129
-117.905
-113.433

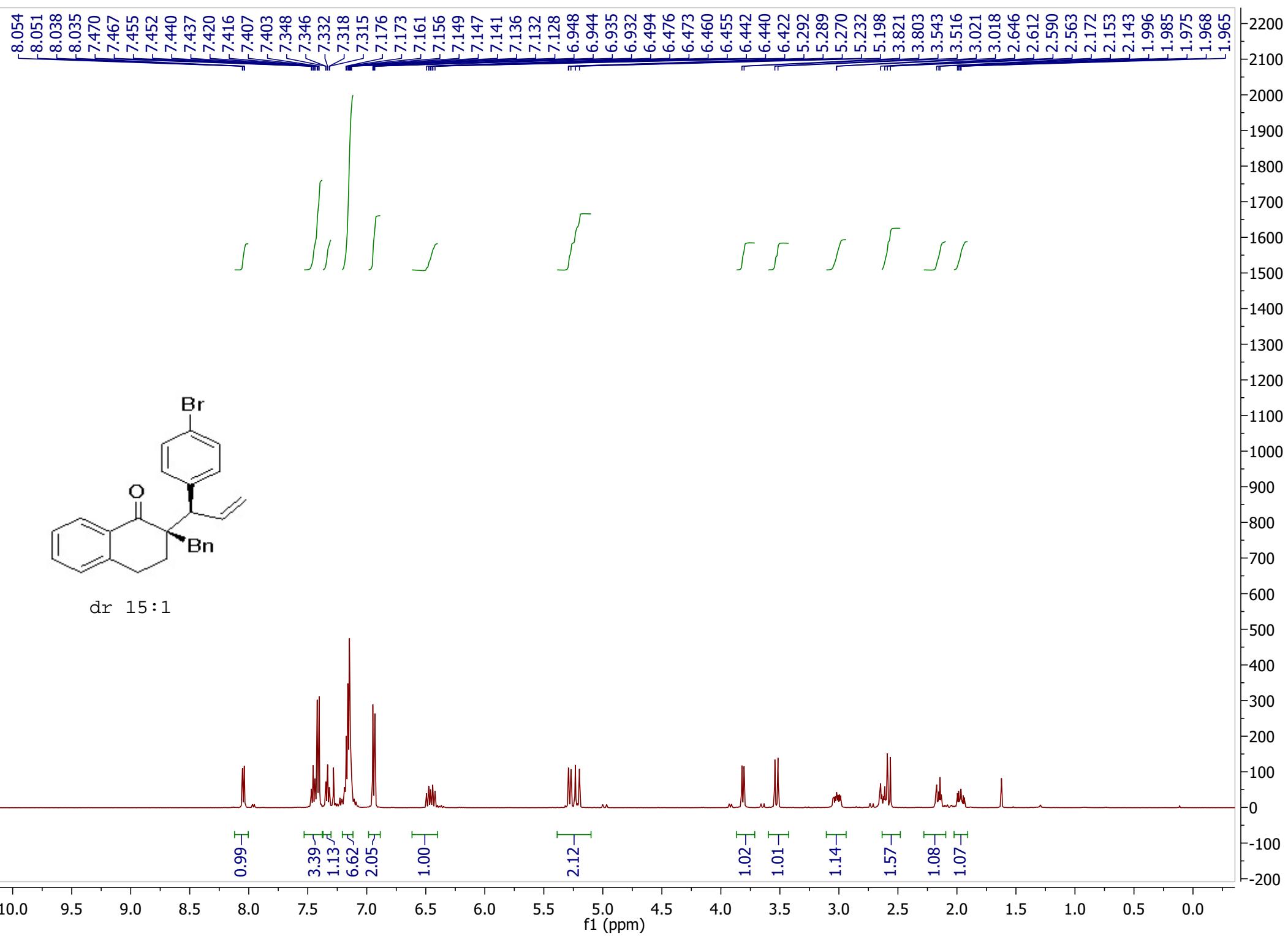
55.167
53.857
53.264

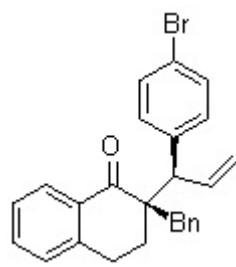
-39.343
-28.941
-25.070











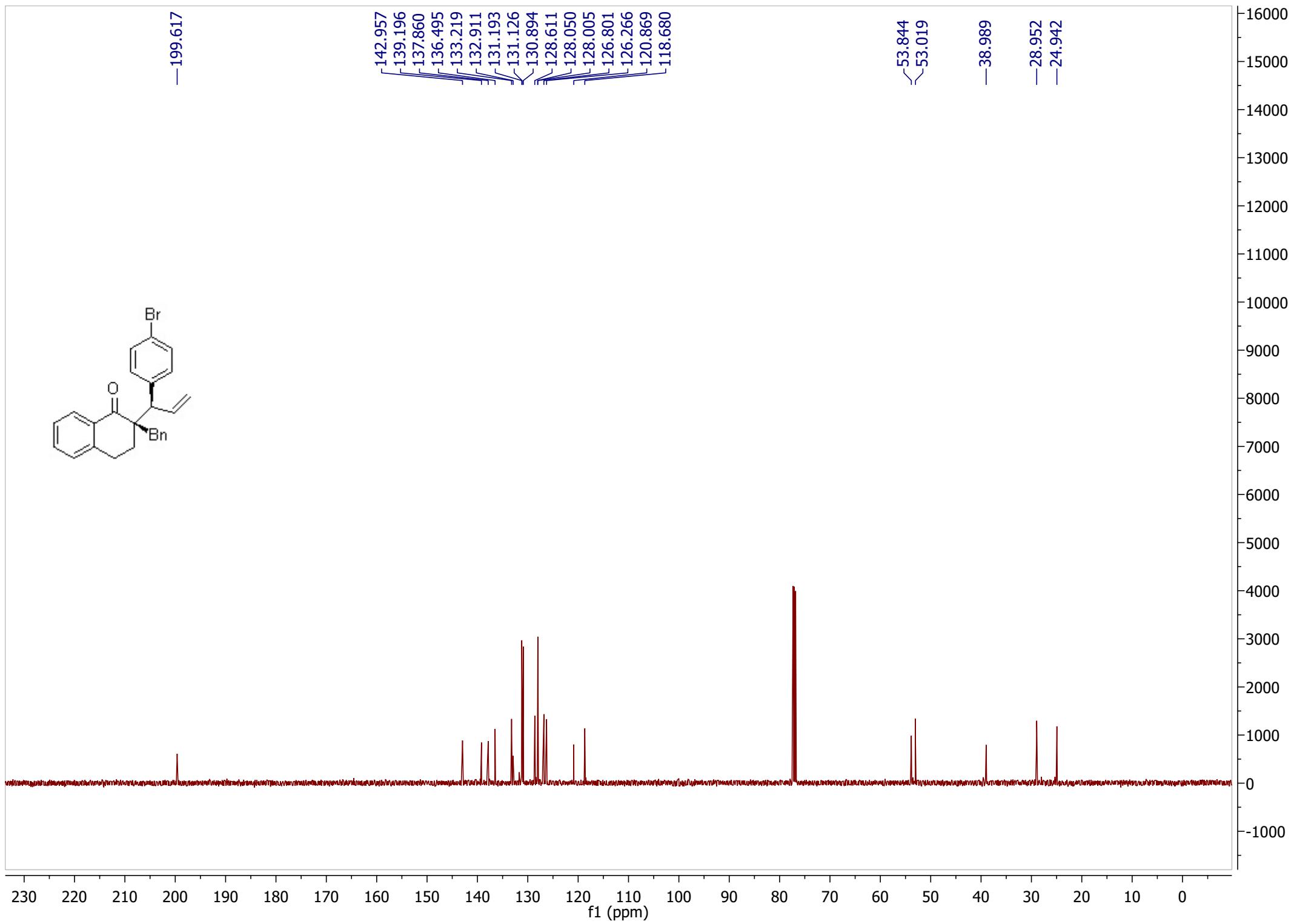
—199.617

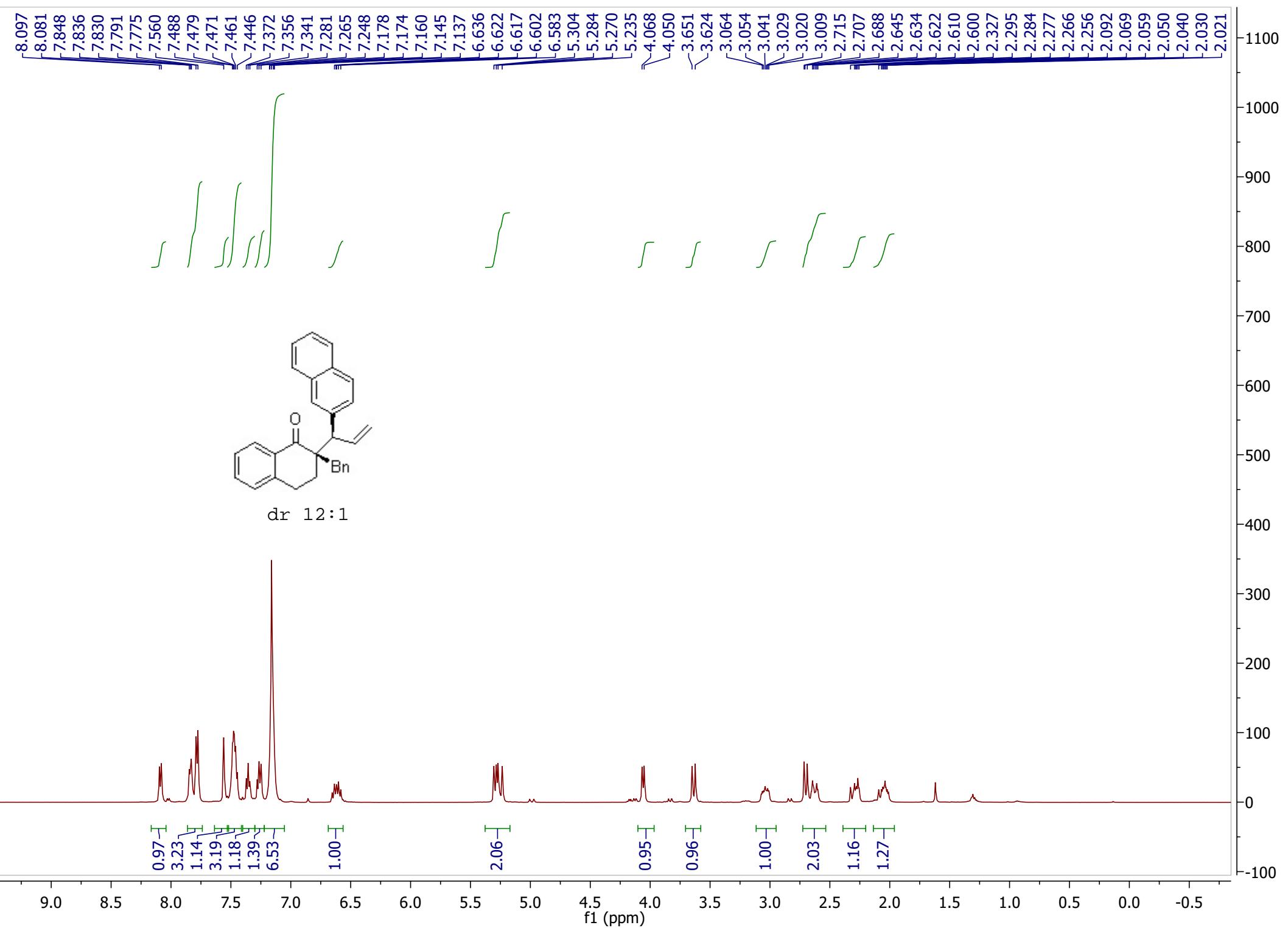
142.957
139.196
137.860
136.495
133.219
132.911
131.193
131.126
130.894
128.611
128.050
128.005
126.801
126.266
120.869
118.680

53.844
53.019

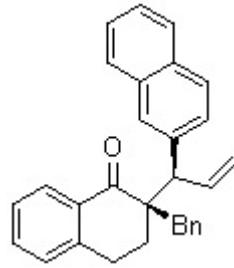
—38.989

—28.952
—24.942





—200.180



143.043
138.095
137.751
137.102
133.299
133.176
133.054
132.390
130.874
128.504
128.412
127.971
127.922
127.784
127.755
127.578
127.440
126.692
126.162
125.928
125.622
—118.334

—55.107
~53.375

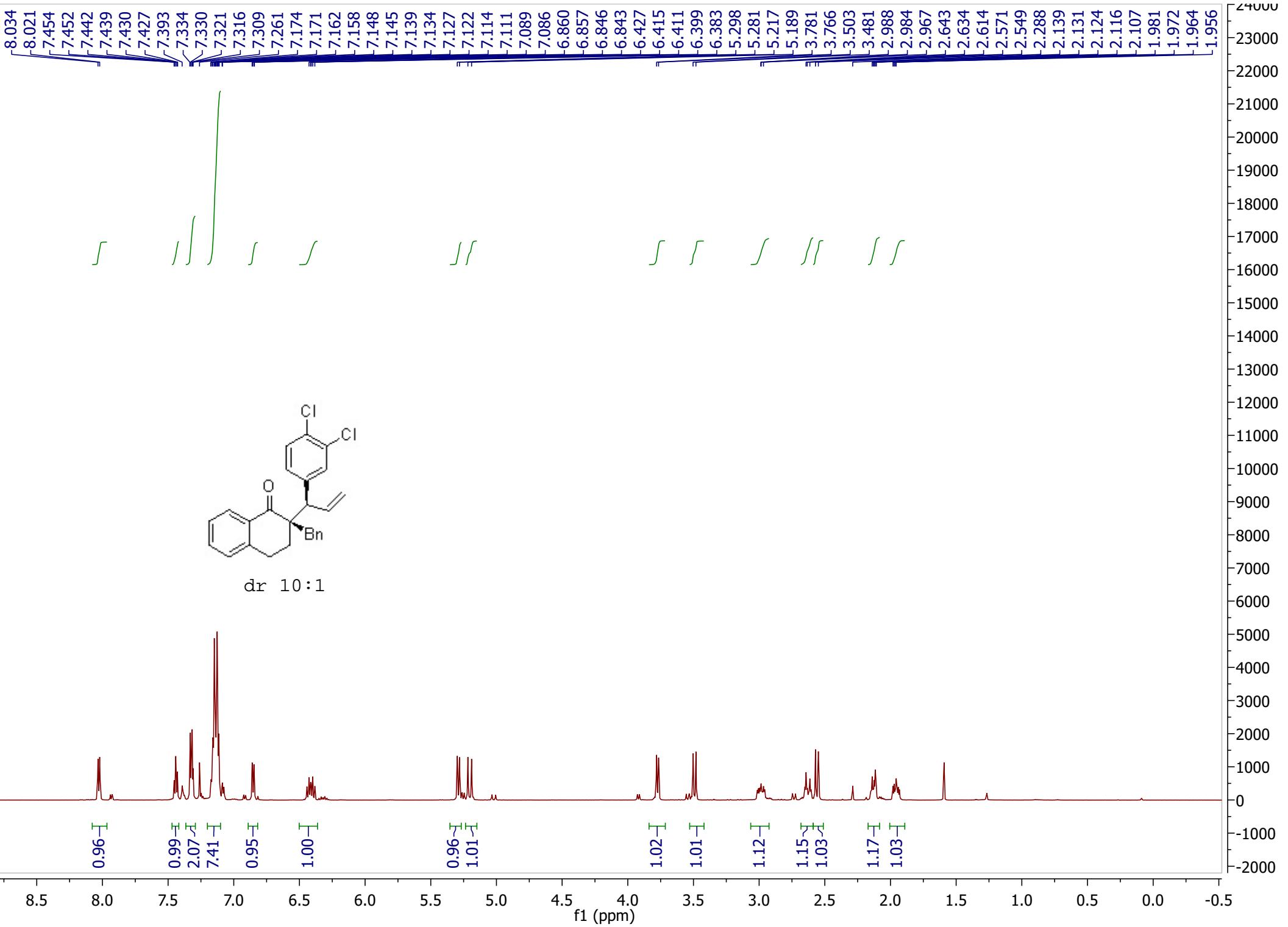
—39.813

—29.017
—25.150

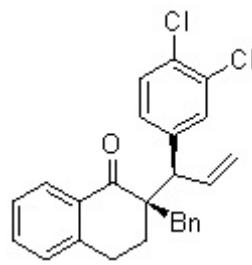
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2



-199.410



142.807

140.496

137.526

135.989

133.278

132.789

131.968

131.298

130.850

130.808

129.828

128.897

128.559

128.006

127.992

126.846

126.313

-119.059

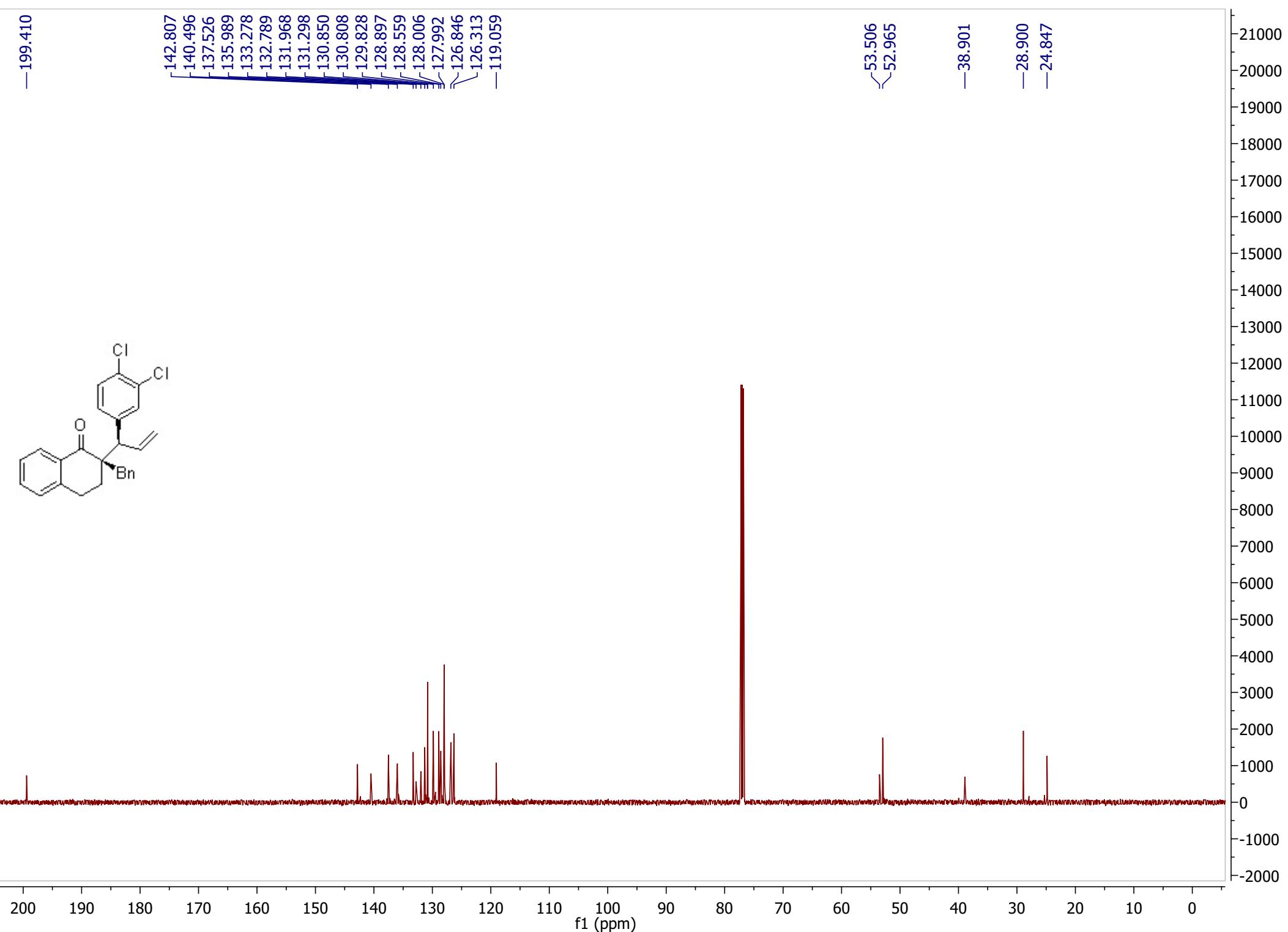
53.506

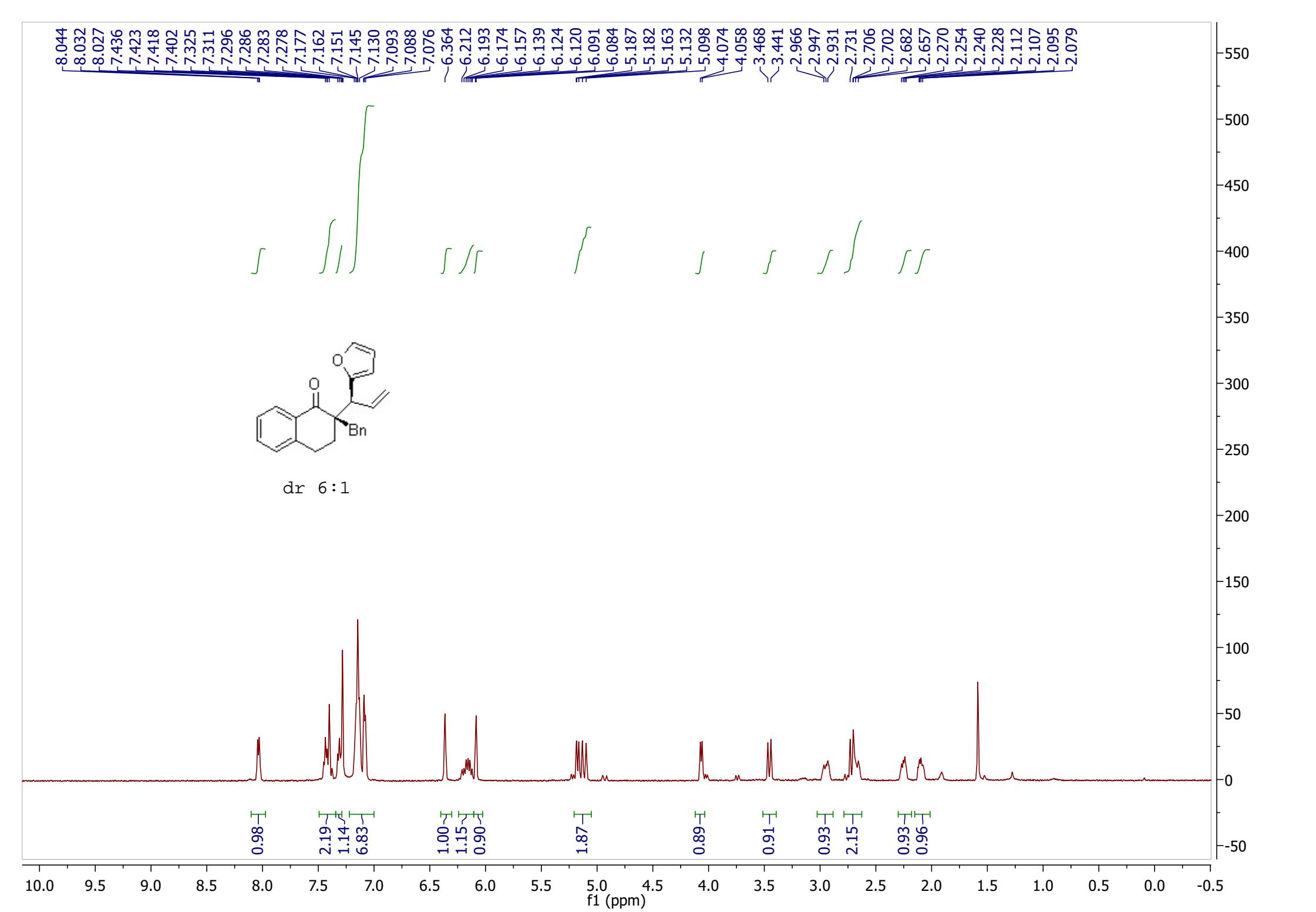
52.965

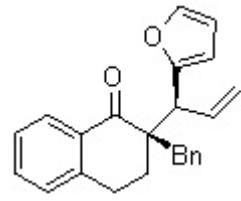
-38.901

-28.900

-24.847



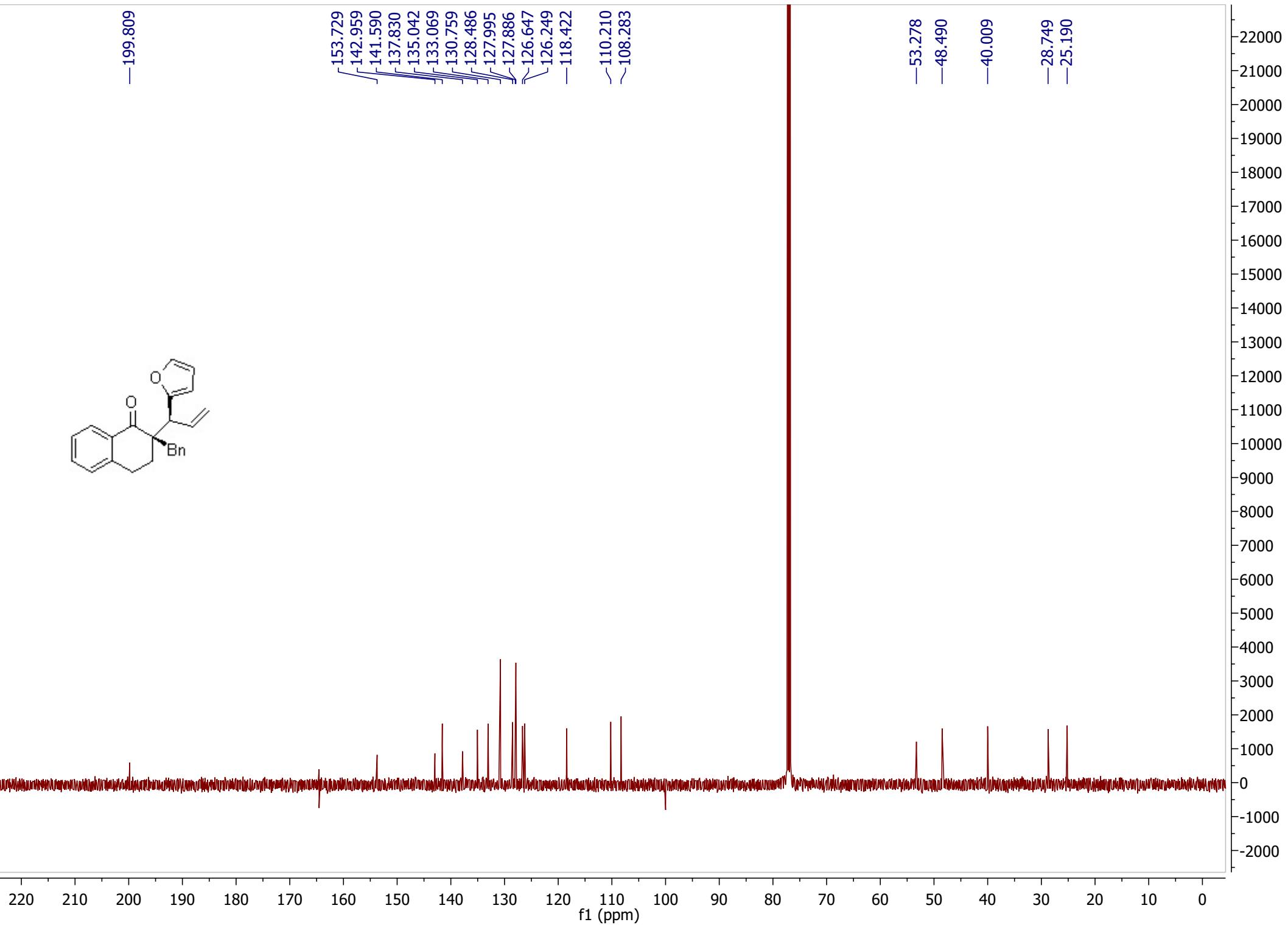


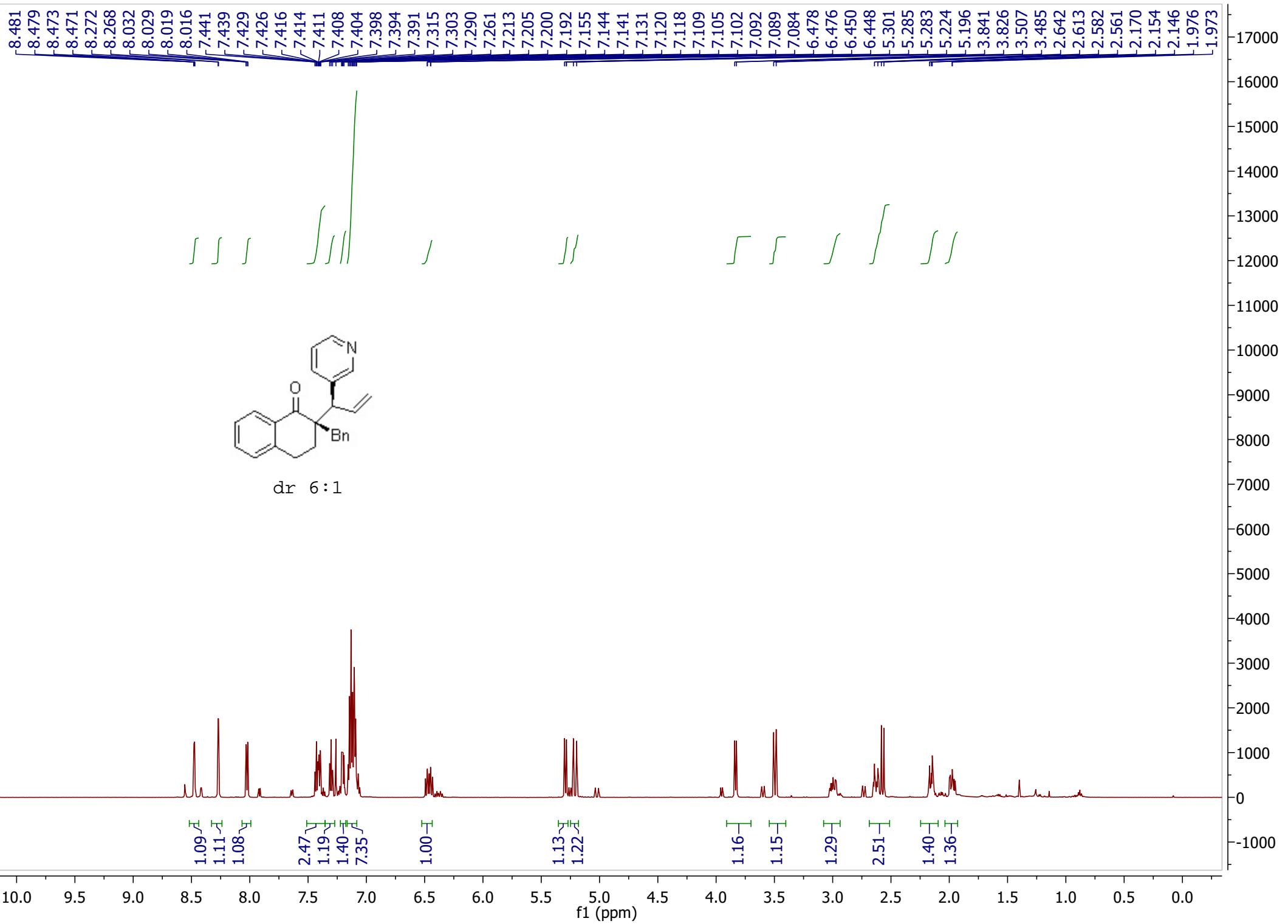


—199.809

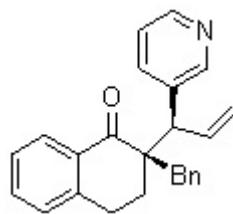
153.729
142.959
141.590
137.830
135.042
133.069
130.759
128.486
127.995
127.886
126.647
126.249
—118.422
—110.210
—108.283

—53.278
—48.490
—40.009
—28.749
—25.190





-199.366

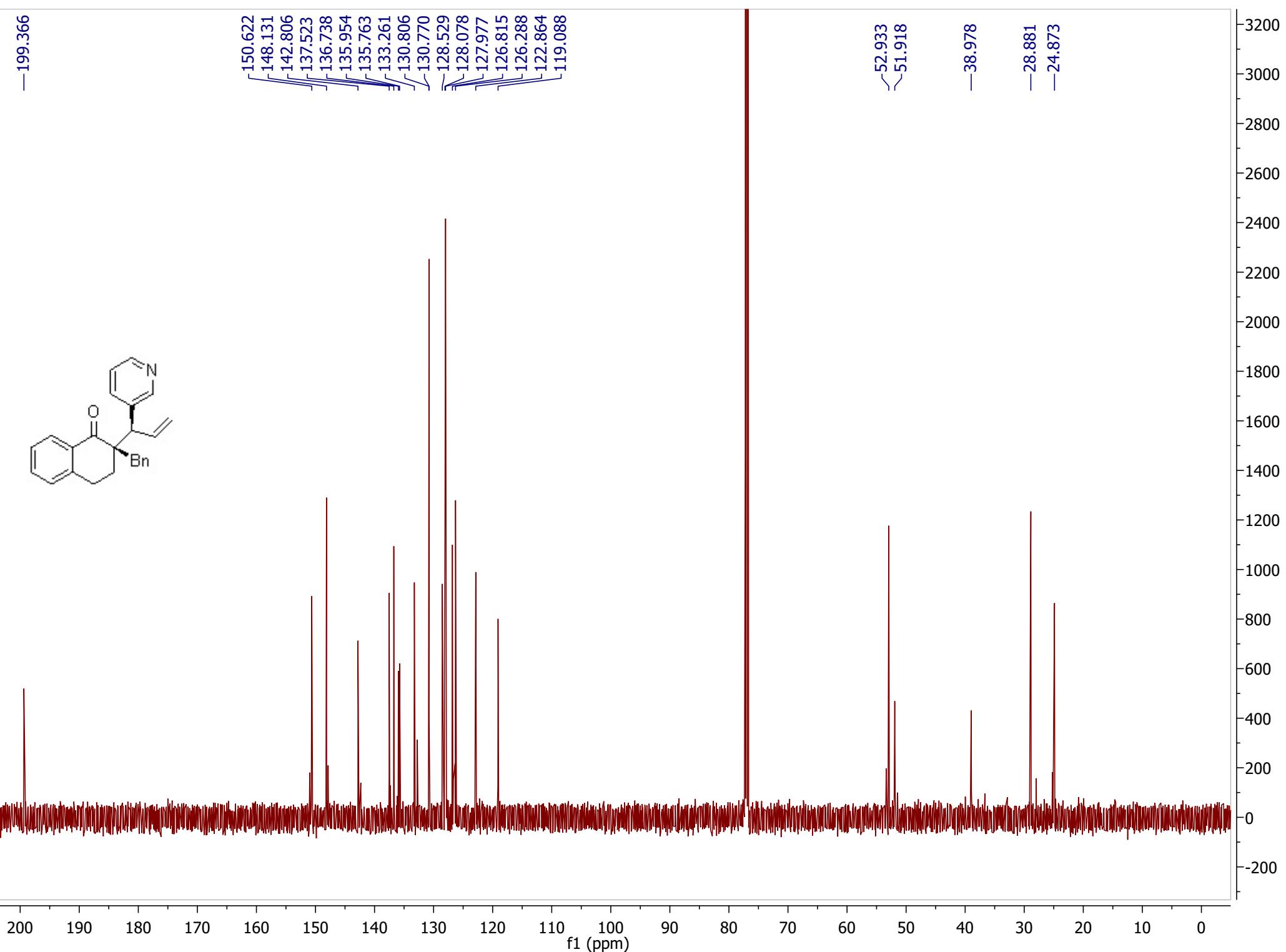


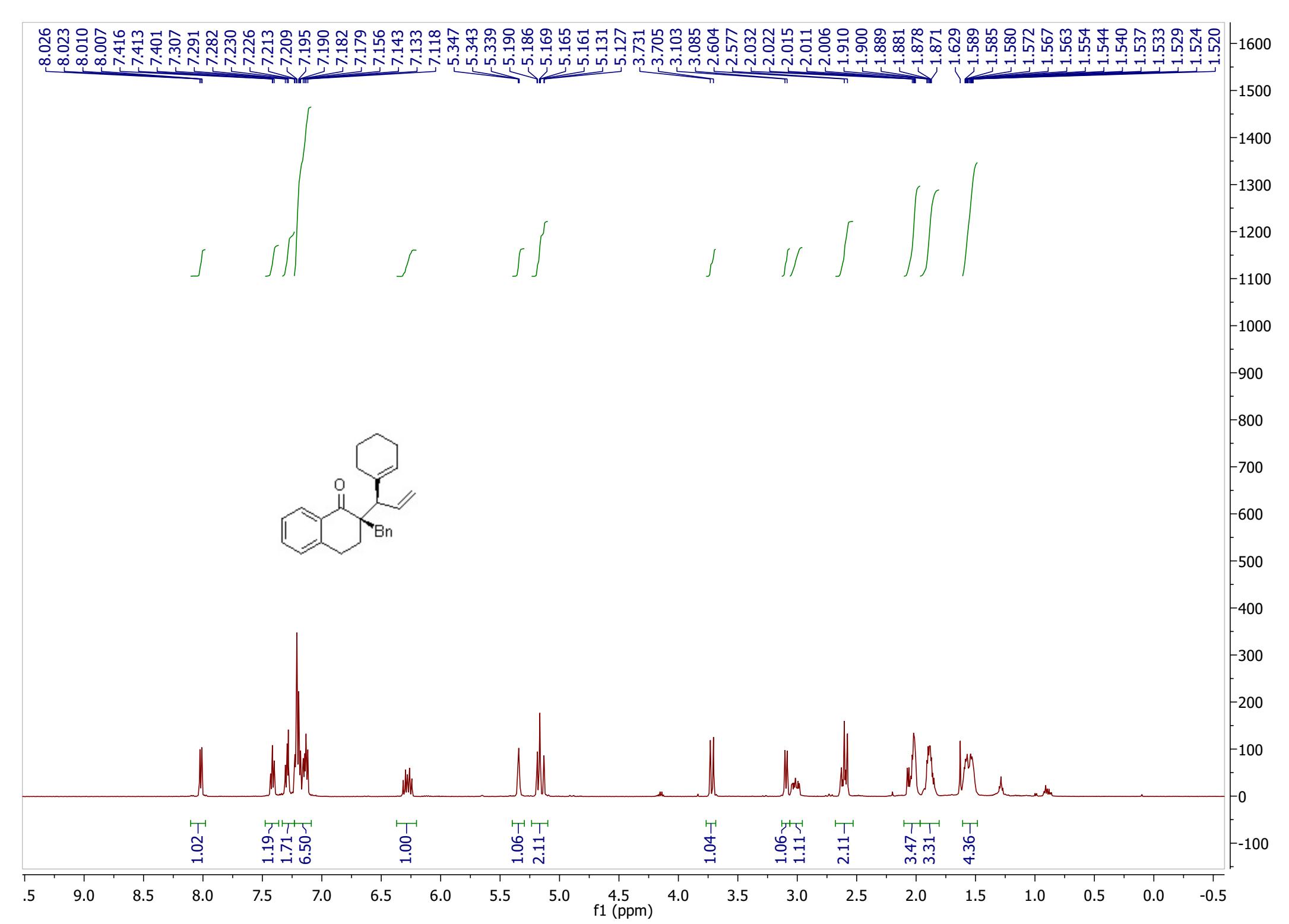
150.622
148.131
142.806
137.523
136.738
135.954
135.763
133.261
130.806
130.770
128.529
128.078
127.977
126.815
126.288
122.864
119.088

52.933
51.918

-38.978

-28.881
-24.873



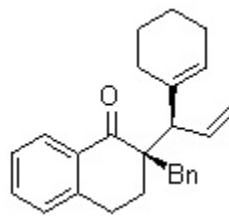


-200.551

142.915
138.598
137.302
136.795
133.263
132.794
130.977
128.461
127.904
126.545
126.137
126.058
-116.529

-39.096
-29.312
-28.999
-25.463
-25.088
-23.094
-22.298

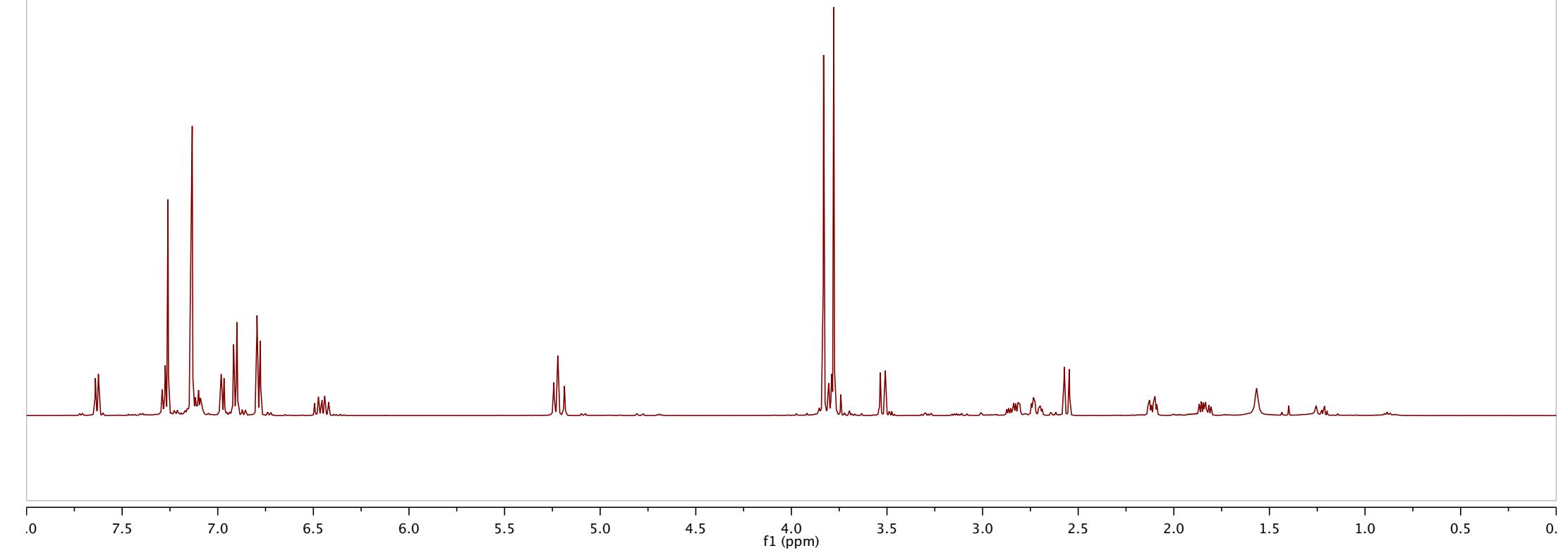
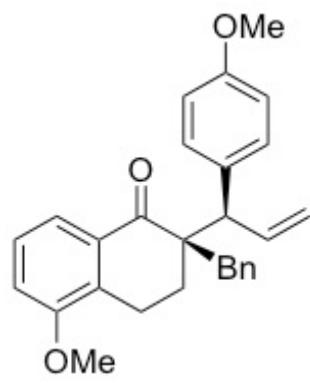
-56.151
-52.560

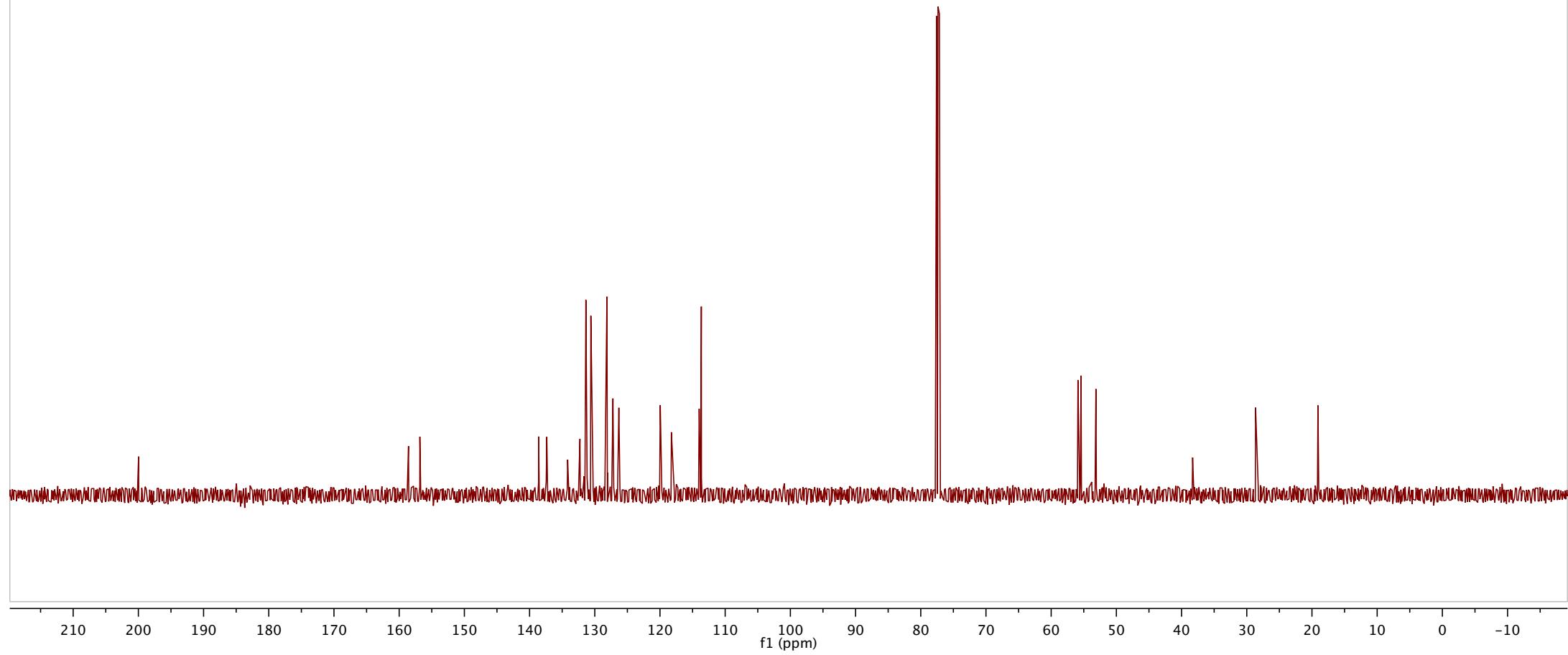
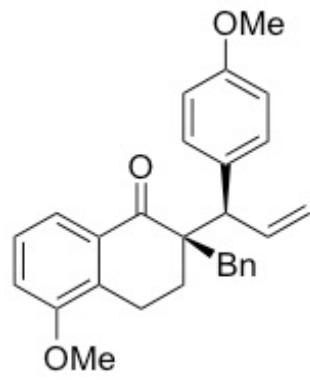


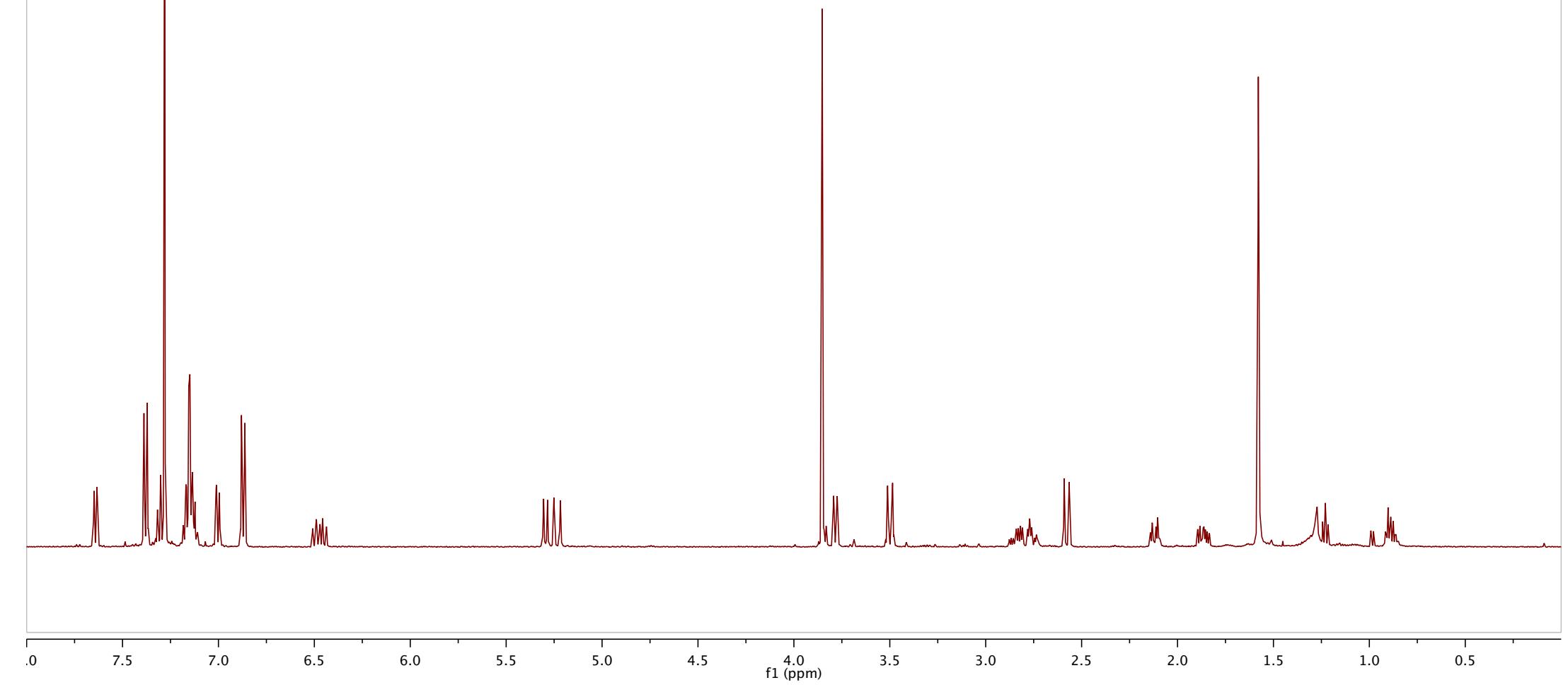
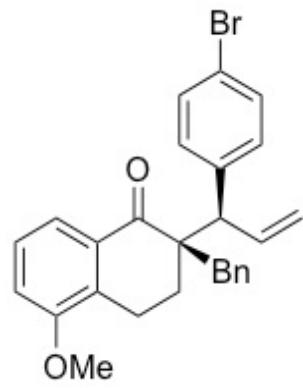
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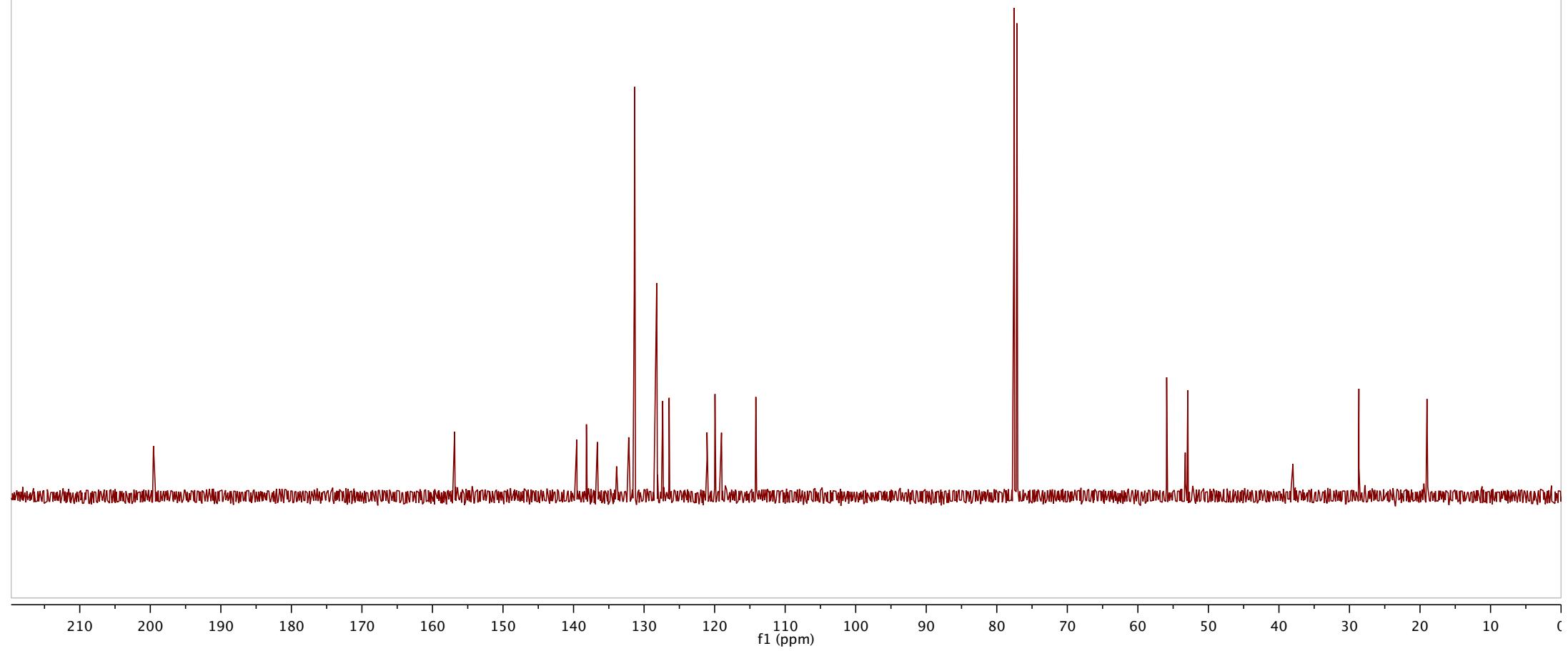
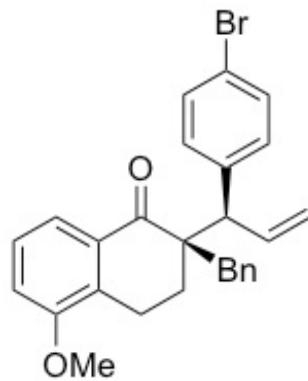
f1 (ppm)

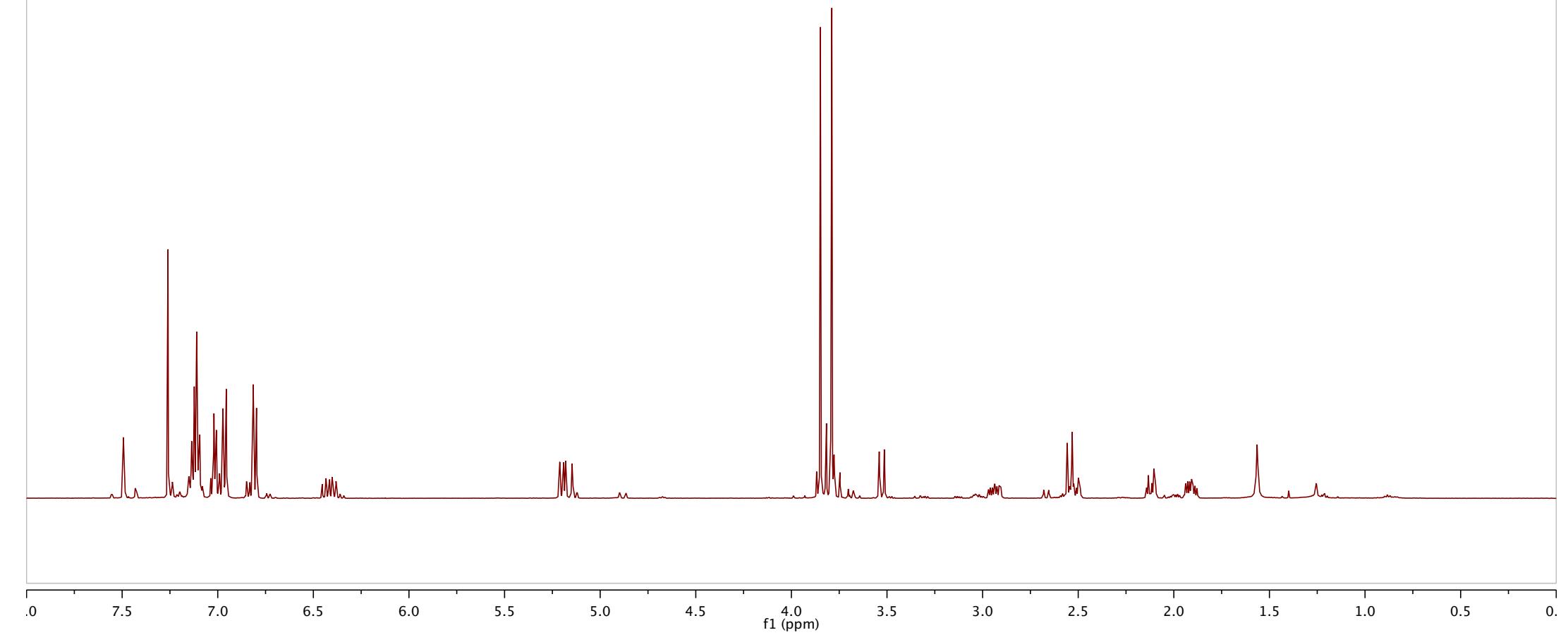
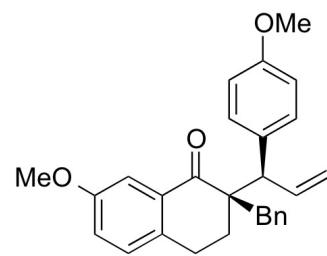
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

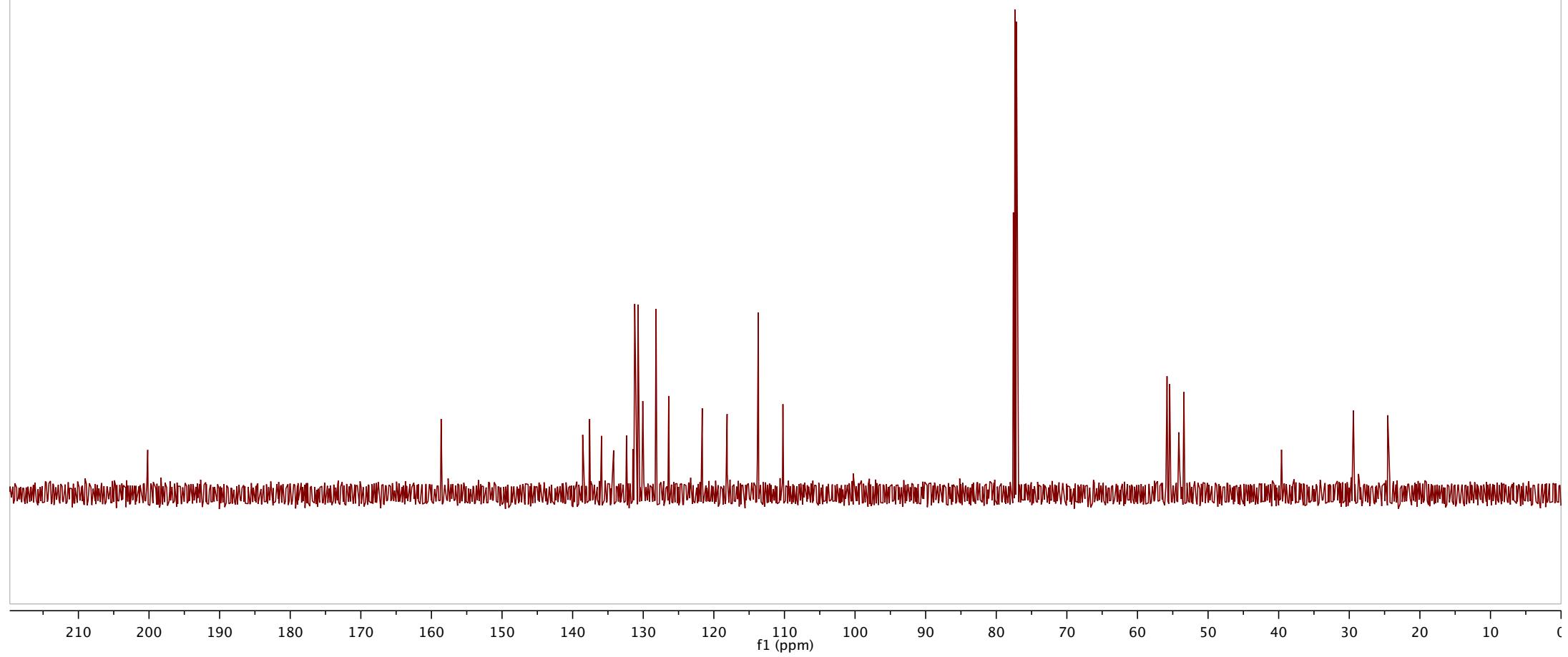
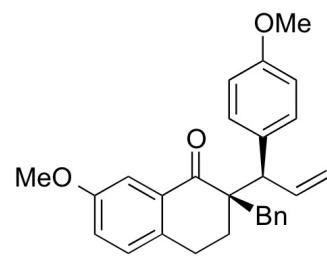


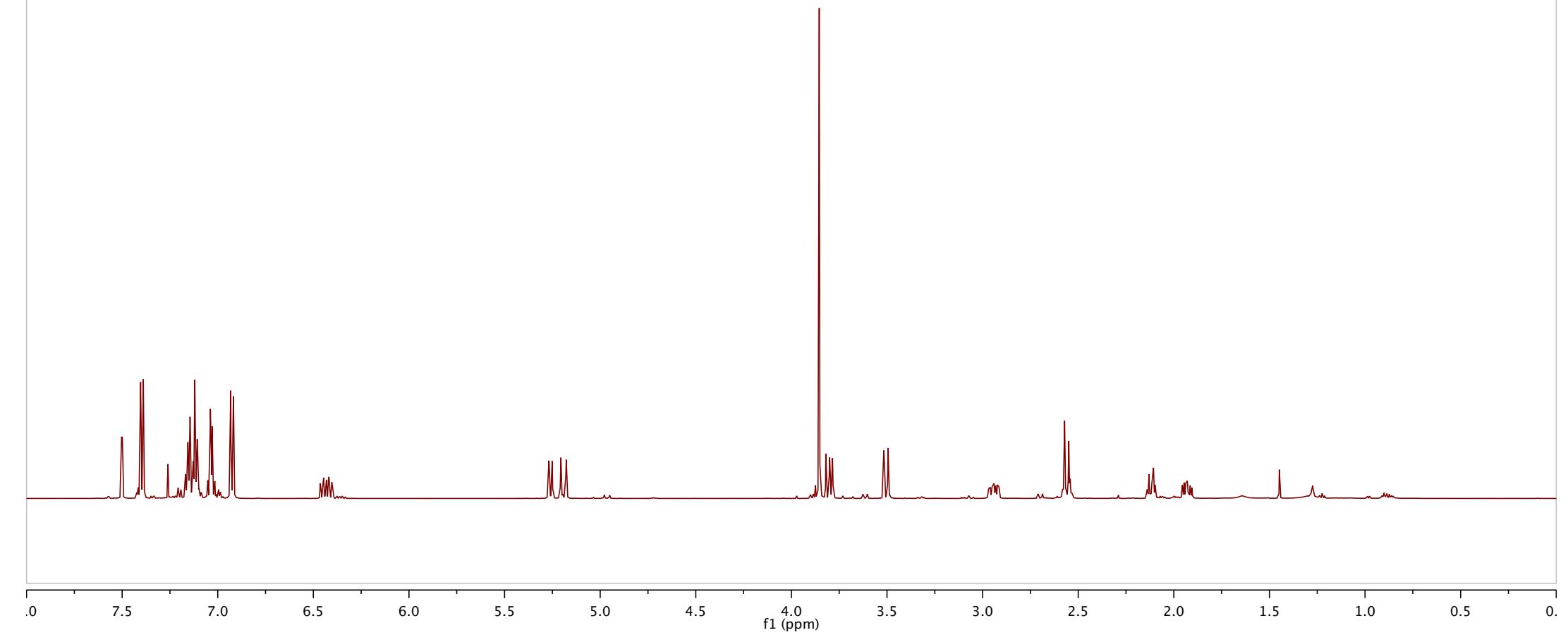
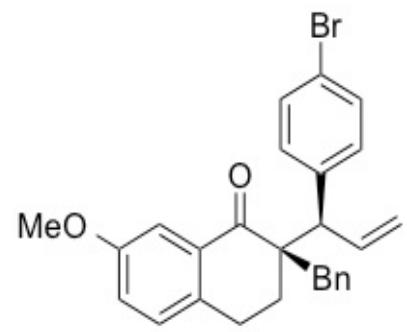


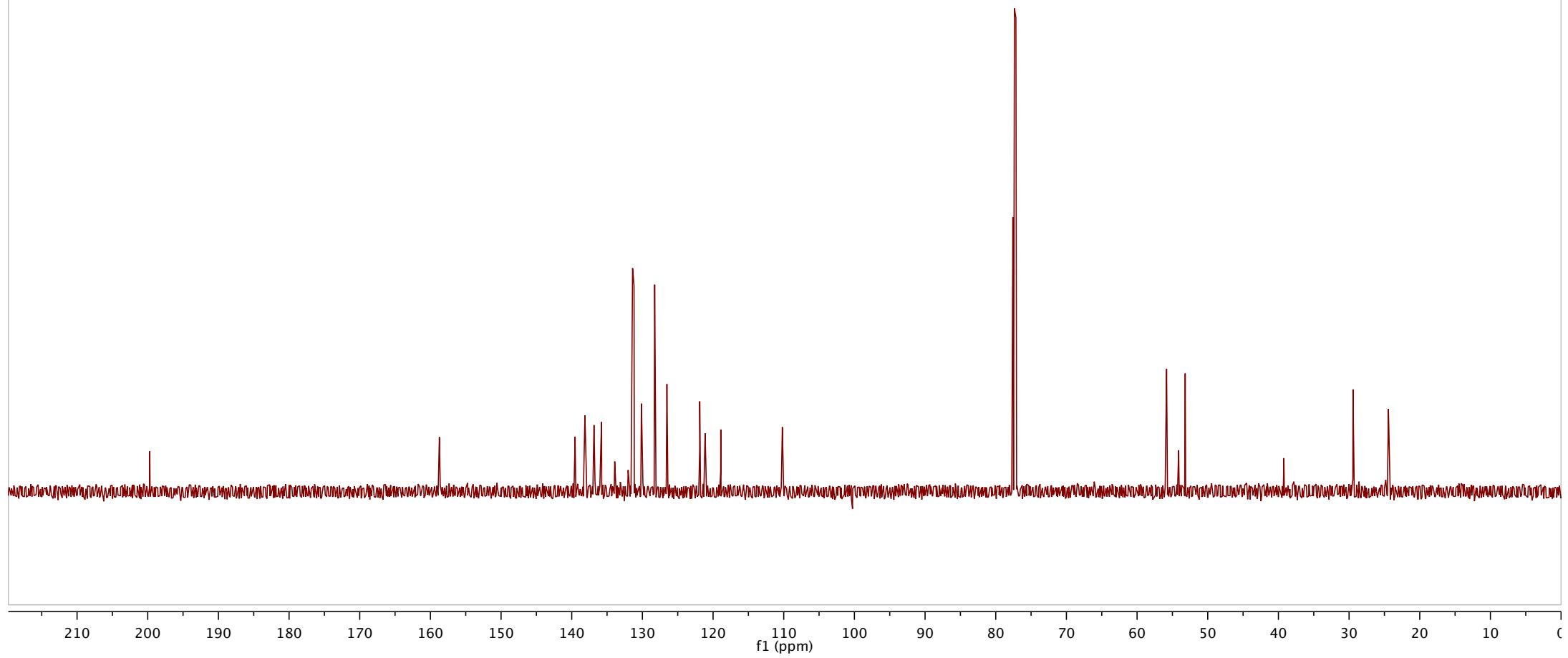
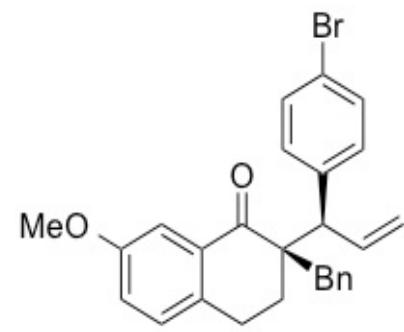


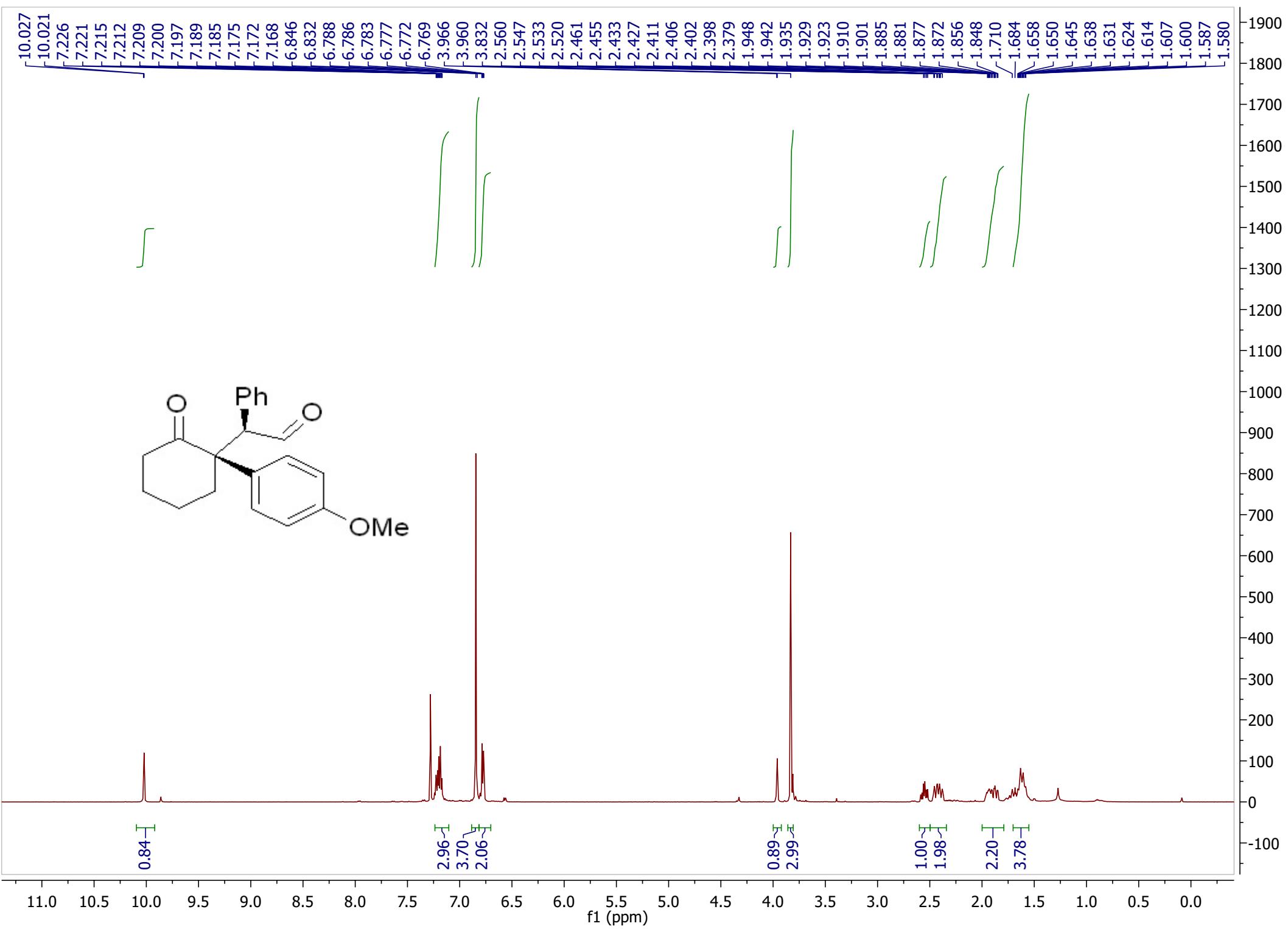












—213.036

—200.389

—158.846

134.118
131.332
130.112
128.072
127.725
127.242

—113.675

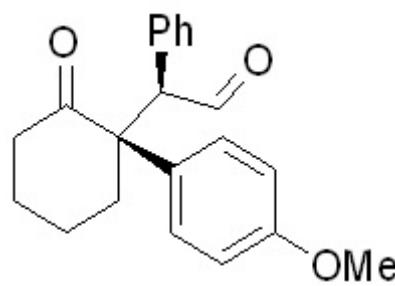
~63.935
~61.686
~55.199

—39.801

—36.959

—28.385

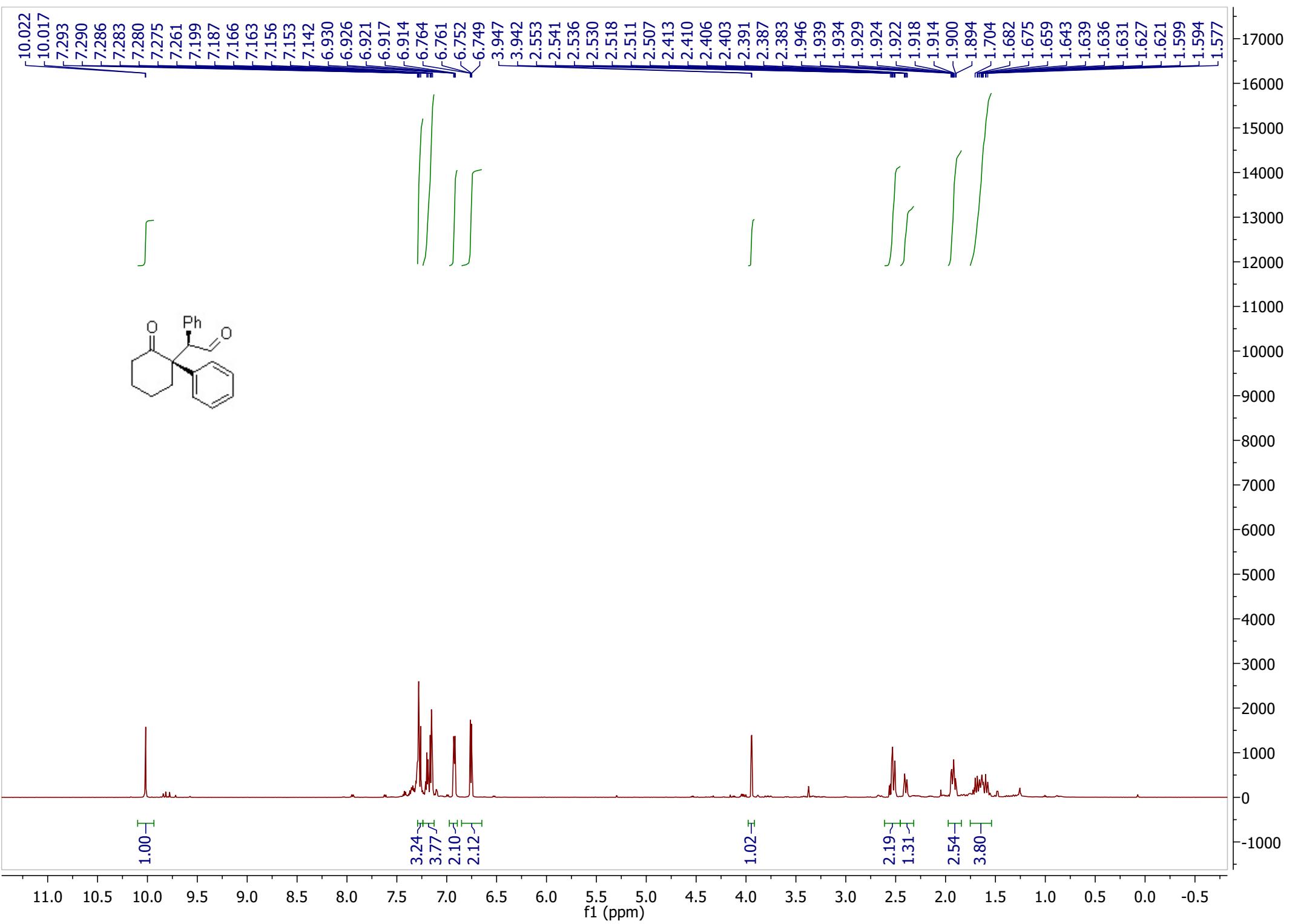
—20.907



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

9000
8000
7000
6000
5000
4000
3000
2000
1000
0



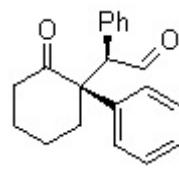
-212.882

-200.350

136.381
134.071
131.323
128.929
128.350
127.740
127.564
127.270

-63.980
-62.523

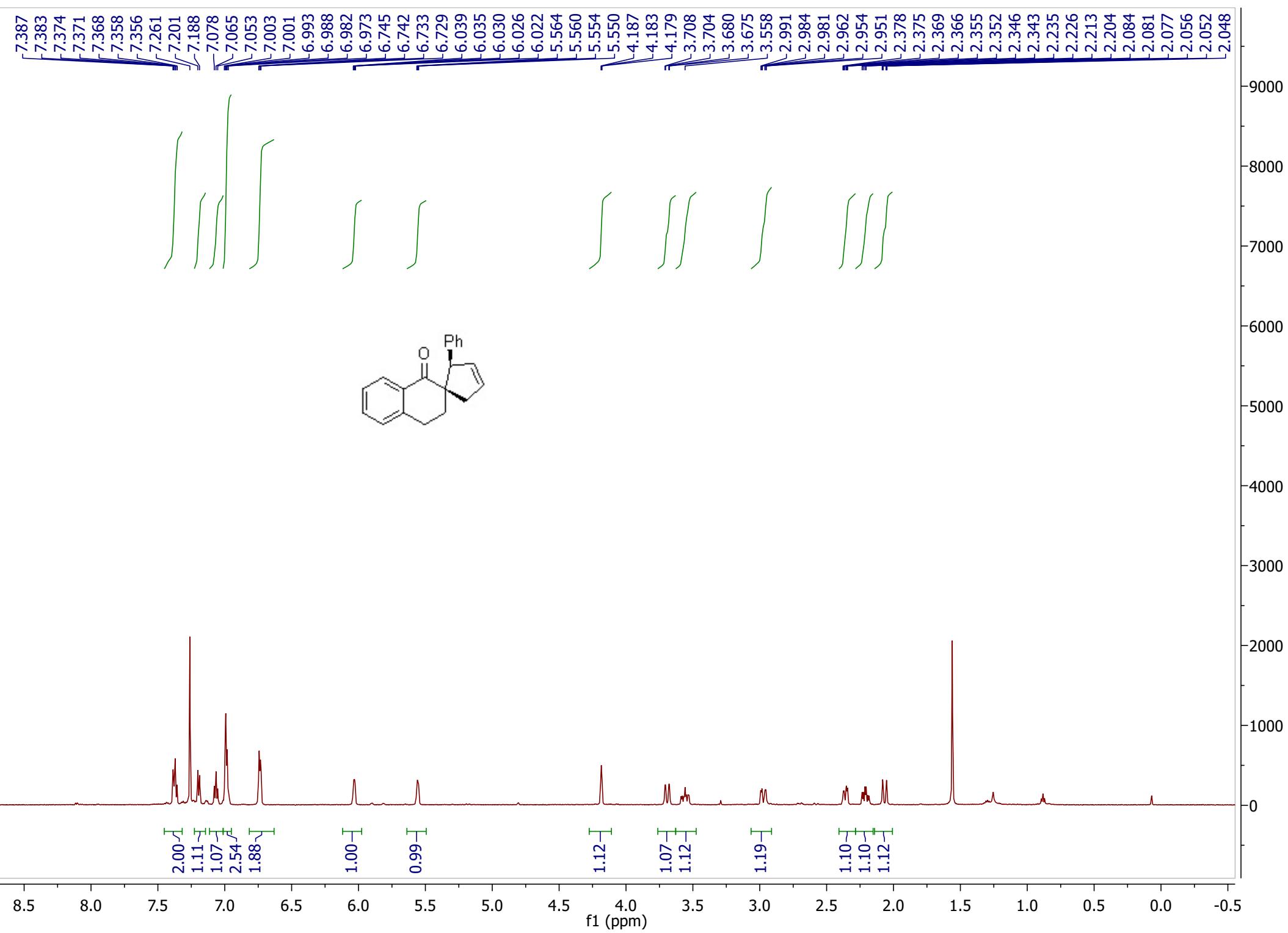
-40.010
-36.823
-28.429
-21.016



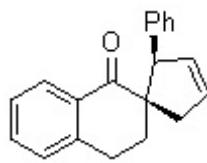
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000



-199.311



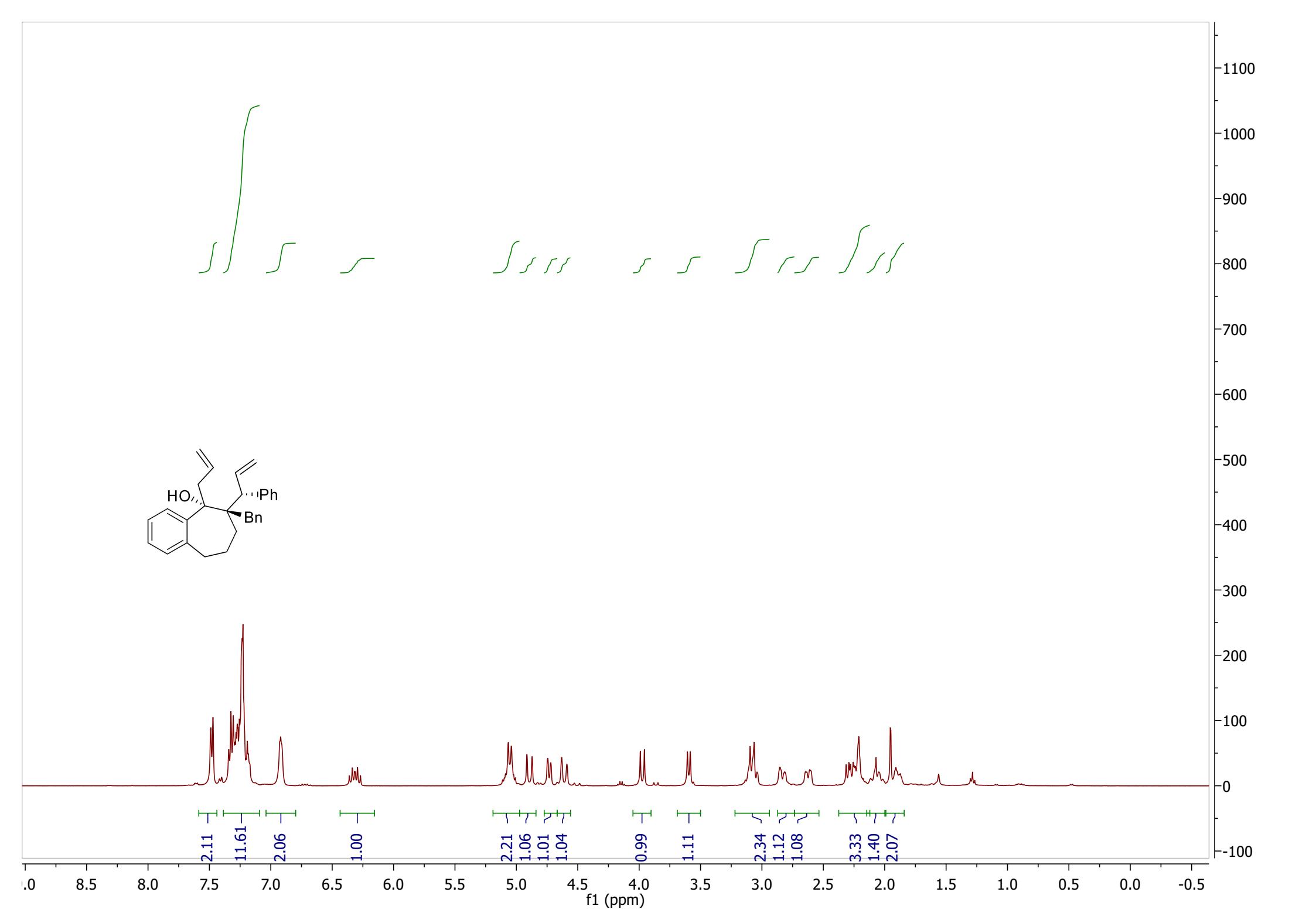
141.962
139.558
133.433
132.525
130.742
130.183
128.625
128.244
127.535
127.456
126.488
126.173

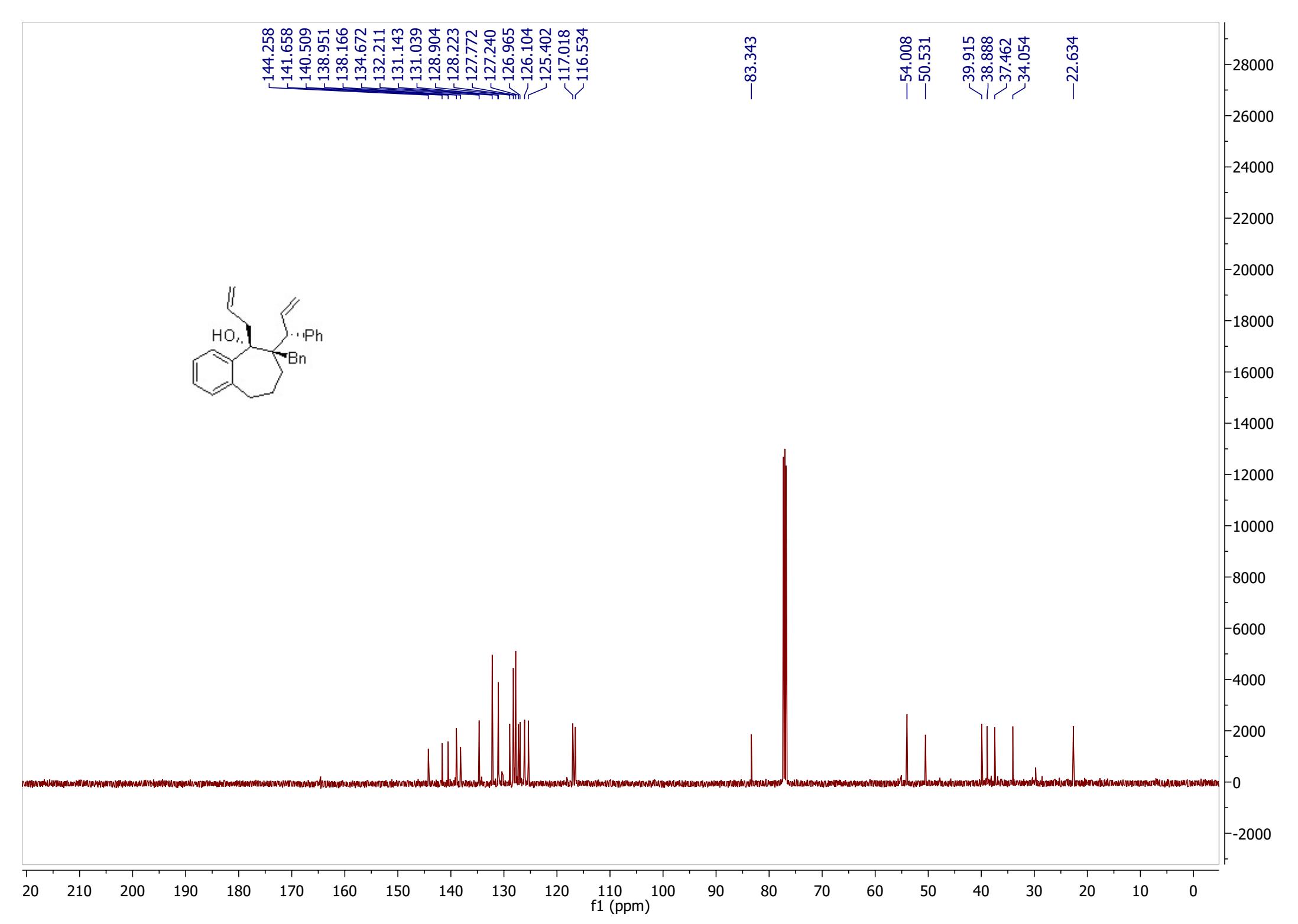
57.342
57.065
-41.908
-35.409
-25.375

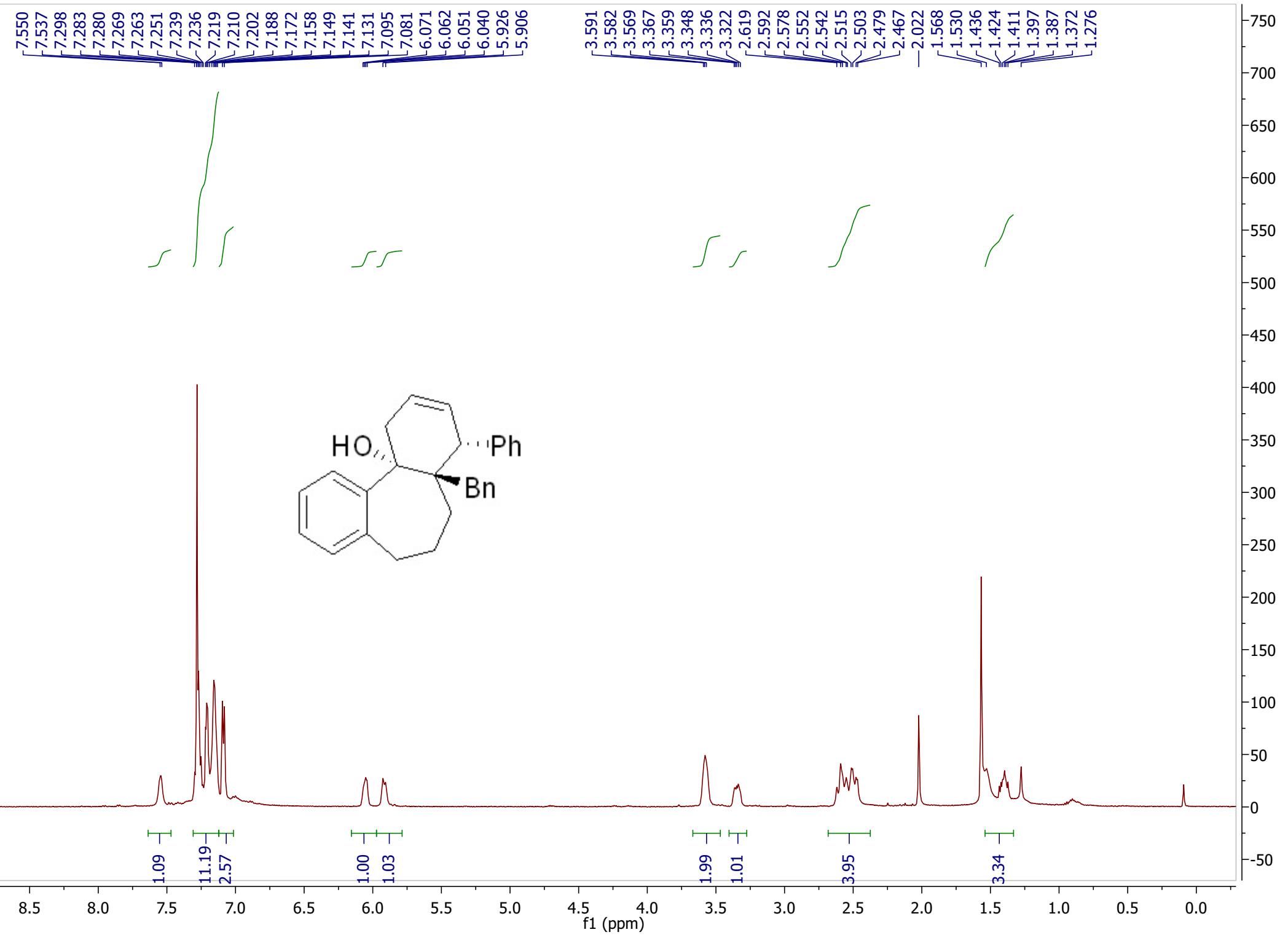
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

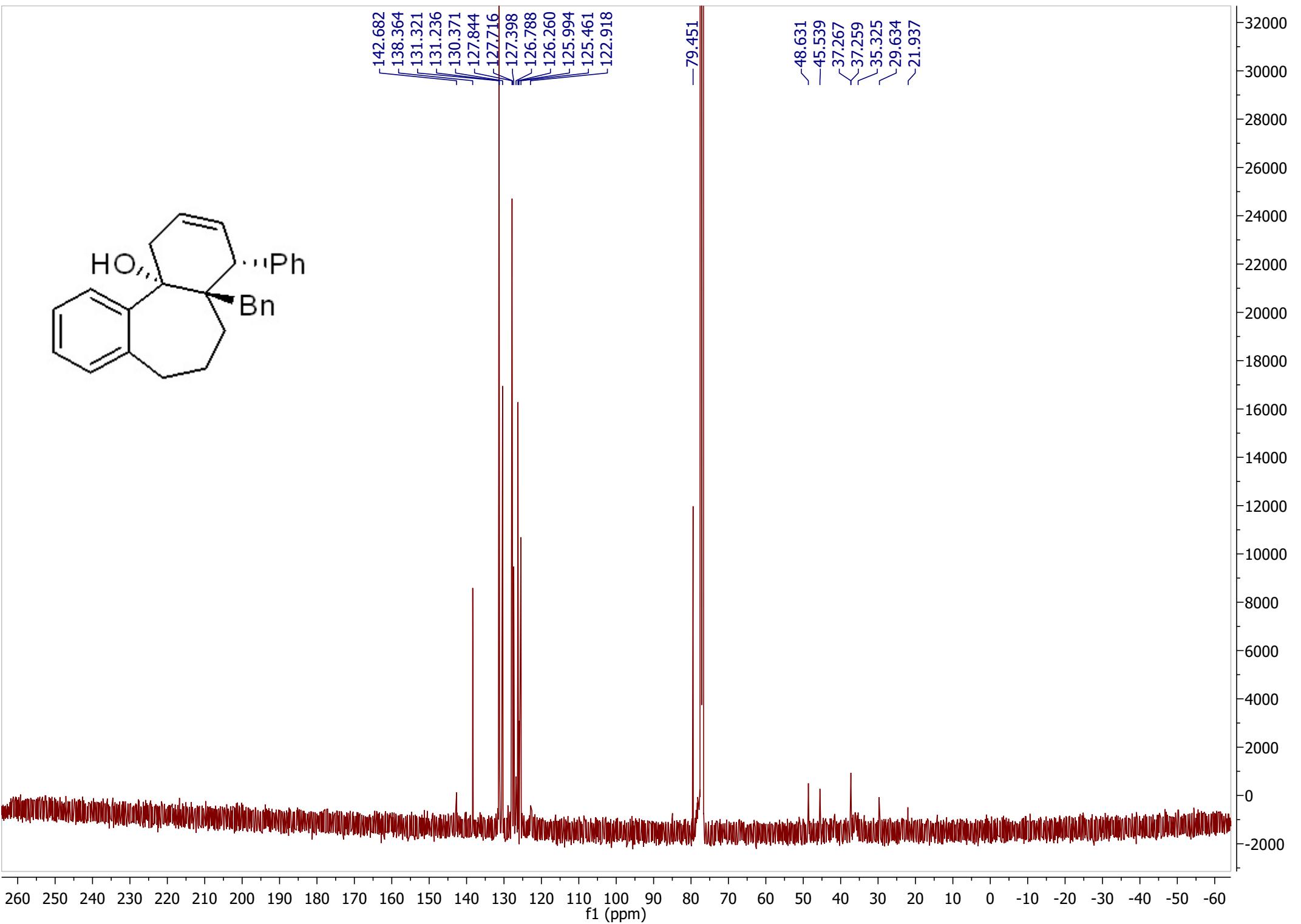
f1 (ppm)

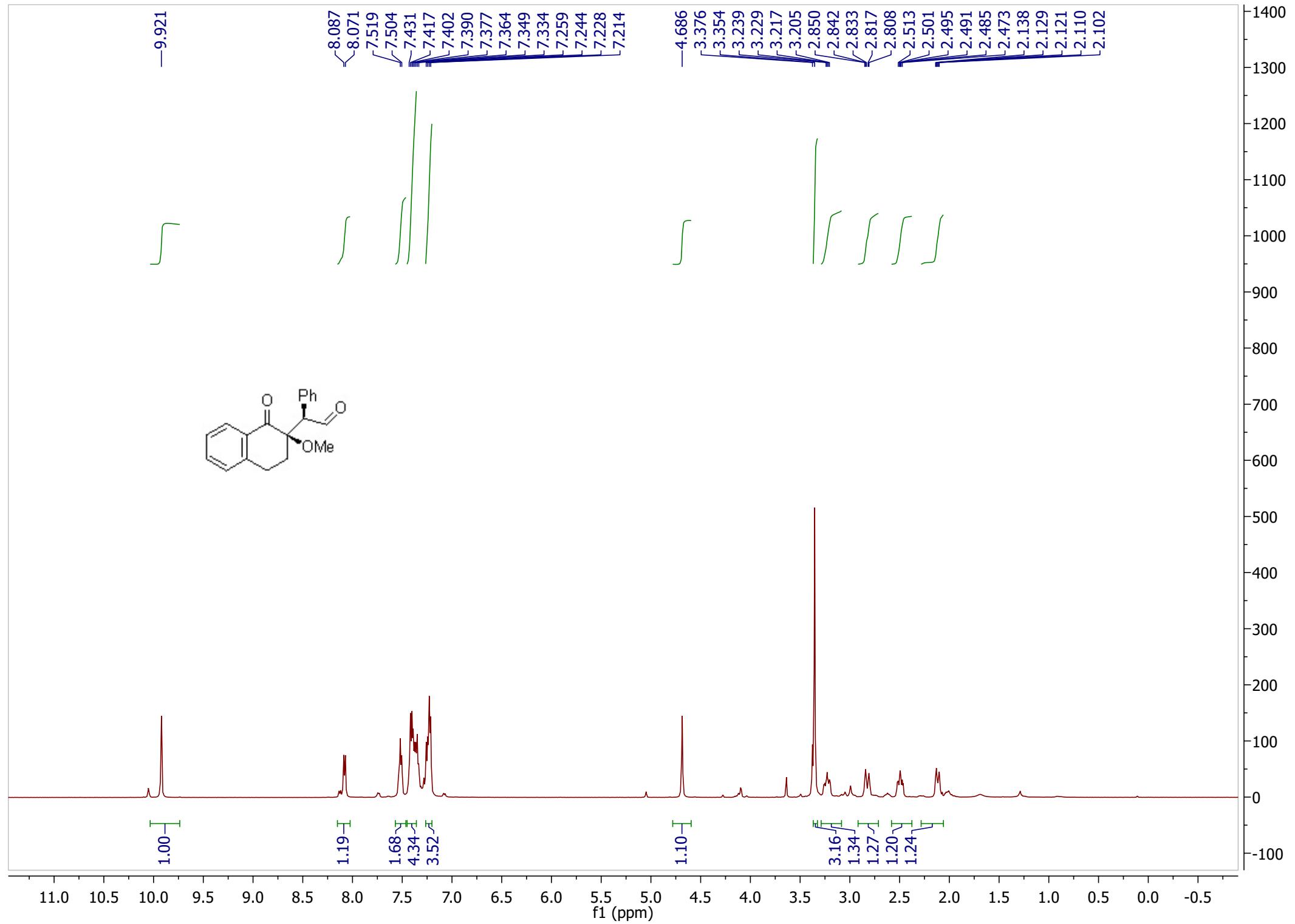
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

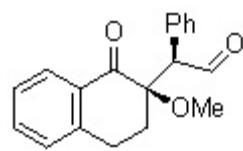












—199.322
—194.411

—144.031
—133.891
—131.921
—131.280
—130.986
—128.760
—128.693
—128.339
—128.048
—126.733

—80.526

—57.869
—51.999

—30.084
—24.784

